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## VARIOUS MODES OF ATTACK IN CRYSTALLOGRAPHIC INVESTIGATIONS

J. D. H. DONNAY, *The Johns Hopkins University*, G. TUNELL,  
and T. F. W. BARTH, *Geophysical Laboratory of  
the Carnegie Institution of Washington*.

### INTRODUCTION

The scope of this paper lies wholly in geometrical and structural crystallography. It is concerned only with the directions of the *crystal planes*, expressing the five known discontinuous vectorial properties of crystals, that is to say: rate of growth, cohesion, twinning, gliding, and *x-ray* diffraction. The corresponding planes, evidence of these properties, are: the faces, cleavage planes, twinning planes, gliding planes, and *x-ray* "reflection" planes.

The investigation may be carried on with different purposes in view and, accordingly, lead to different kinds of crystal descriptions (axial elements) embodying the results obtained. Three of the principal aims of the crystallographer are: (1) the determination of crystals, (2) their morphological characterization, (3) the study of their intimate structure. A descriptive method suitable for one of these aims will not necessarily fit another purpose.

The determinative description of a crystal stands apart from its morphological and structural descriptions. The relation between the last two is incompletely known, and they cannot be unified as yet. Whether it will ever be possible to do so remains an open question. Certainly, in our present state of knowledge, neither of these two descriptions can be discarded in favor of the other under penalty of leaving experimental facts unexpressed that can be expected to contribute to the elucidation of the relationship between form and structure.

### I. THE GONIOMETRIC DETERMINATIVE METHOD

The aim of this method is to provide a tool for goniometric determination of crystalline substances by means of simple constants, without transformations of angular values into axial elements.

The principal attempt to devise such a method is that of Fedorov.<sup>1</sup> His work, "Das Krystallreich," contains the determinative criteria of several thousands of substances. They were compiled by Fedorov and his co-workers (D. N. Artemyev, T. V. Barker, B. P. Oryelkin, and V. I. Sokolov) over a period of about twelve years. Although determination is actually possible by means of these tables, the method involved is rather complicated and has not met with great success. This is explained by the fact that Fedorov tried to give a single solution to two distinct problems: that of determination and that of morphological characterization. His ambition was to find the "correct orientation" for each crystal. This correctness of orientation was sought in hypothetical considerations about structure. Determinative tables came out as a by-product of the investigation which was in reality primarily morphological. As a result, the determinative end was largely frustrated by unnecessary complications introduced by the morphological viewpoint and the structural hypotheses.

A student of Fedorov, Boldyrev, tried to obviate the difficulties inherent in the Fedorov system and proposed another determinative scheme,<sup>2</sup> stripped entirely of structural or morphological concerns. Its principle is to use the available angular values recorded for crystalline substances without transformation of the adopted orientation (or setting). Several entries in the tables are needed for each substance. The bulk of such determinative tables (already completed in manuscript form for tetragonal, trigonal, and hexagonal substances) would be enormous and hinder their practicability in the systems of lower symmetry.

The latest method, the most satisfactory, is due to T. V. Barker.<sup>3</sup> Here again, the purpose is solely determinative, and admittedly so. Barker gives rules designed to enable any crystallographer to choose a *standard orientation* for any crystal. Angular values are used as determinative criteria, one of the angles is the main classification angle and the substances are listed (in each crystal system)

<sup>1</sup> Fedorov, E. S., *Das Krystallreich; Tabellen zur krystallochemischen Analyse: Mém. Acad. Sci. Russie* (8), vol. 36, Petrograd, 1920.

<sup>2</sup> Boldyrev, A. K., *Principe de la nouvelle méthode de diagnose cristallographique de la matière: Mém. Soc. Russe Min.* (2) vol. 53, pp. 251-337, 1924. (Russian text, French summary.)

<sup>3</sup> Barker, T. V., *Systematic Crystallography: an essay on crystal description, classification and identification, 1930, London, Thomas Murby and Co., 1 Fleet Lane, E.C. 4.*



according to increasing values of that angle. The rules set for that purpose may appear a little arbitrary but arbitrariness is here entirely justifiable when it leads to an easy determinative scheme.

The first principle advocated by Barker is that of "simplest indices." He calls 0 and 1 "simplest" indices, and all indices higher than 1, "complex" indices. The first step in the determination of a crystal is to plot its stereographic projection from the measured angular values, then to find which orientation of the crystal will permit assignment of "simplest indices" to the largest number of observed forms. On any crystal, twenty-six faces at the most can be given simplest indices; Barker calls them (by analogy with the isometric nomenclature) the six *cubic* faces, the twelve *dodecahedral* faces, and the eight *octahedral* faces. Often, there is only one orientation leading to a maximum of simplest faces among the observed faces. When ambiguity arises, however, Barker proposes *auxiliary rules* to decide between alternative solutions that leave an equal number of faces with complex indices.<sup>4</sup> When it has been decided which faces are to become "cubic," which "dodecahedral," and which "octahedral," then *ipso facto* the directions of the axes and the axial ratios are fixed, but several possibilities remain as to the naming of the axes and their orientation. As to their names, three cyclic permutations are permissible, which will leave the system of coordinates right-handed (the usual convention of crystallographers at the present time); as to their signs, each one of the eight octants may be selected as "first octant"; hence there is a total of 24 alternatives. Barker first gives rules for naming the axes, then for directing them. Common sense prevails throughout his work; his chief concern is avowedly to make his rules practical and as much in accordance with previous conventions as possible. To illustrate this point, it may be noted that he retains the symmetry axis in the monoclinic system for the *b*-axis, although it would be more logical to make it the *c*-axis; he remarks that "it is 3000 substances too late" to introduce a change in this practice. Similarly, he uses a system of standard letters for form notation, reflecting the common usage outside of French-speaking countries; at the same time

<sup>4</sup> In several cases, the rules given by Barker in his essay have been found to be insufficient. The rules must be recast to meet such cases. A set of New Auxiliary Rules has been suggested. Terpstra, Donnay, Mélon, van Weerden, Studies on Barker's determinative method of systematic crystallography, *Zeit. f. Krist.*, vol. 87, pp. 281-305, 1934.

he states that the French system of form symbols (so-called Lévy notation) undoubtedly is the most logical.

Barker's classification angles are the six angles:

*cr, ra, am, mb, bq, qc*

between the following faces:

*a(100), b(010), c(001), r(101), m(110), q(011).*

Note that the forms may not all be observed forms. Five angles would be sufficient in the most general case (triclinic system), but Barker prefers to list one superfluous angle as a confirmation. In the other crystal systems, he reduces the number of classification angles: four in the monoclinic, three in the orthorhombic, one in the hexagonal, rhombohedral, and tetragonal systems.

The method may be said already to have withstood the test of experience. Barker died without having had time to carry on to completion his highly original work. His determinative tables were only started. Since then, however, Haan<sup>5</sup> has published tables covering 950 substances, which belong to all crystal systems, and has demonstrated the value and practicability of the Barker determinative method. Other workers are now compiling the complete tables, Professor H. L. Bowman, Miss Mary W. Porter, Mr. R. C. Spiller, and Mr. Powell (Oxford), Mr. Max H. Hey (London), Dr. P. Terpstra and his students (Groningen), and Dr. J. Mélon (Liège). Professor Bowman in Oxford will edit the tables, in which the data given by Haan will be incorporated. The Barker system is simple enough to be mastered by any chemist after a short introduction to geometrical crystallography and crystal measurement. Either one-circle or two-circle goniometry is applicable with nearly equal facility. Calculations are reduced to a minimum, since many computations are replaced by graphic determinations on the stereographic net. The duration of a determination ordinarily ranges from half an hour to four hours. This method will make *crystallochemical analysis* a valuable tool for chemists.

## II. THE MORPHOLOGICAL DESCRIPTION OF CRYSTALS

The purpose of a morphological description is to refer the crystal to that set of axial elements which will yield as much information as possible about the presence and respective importance of observed forms, about the habit and, eventually, about the pseudo-symmetry.

<sup>5</sup> Haan, J. H., *Kristallometrische Determineeringsmethoden*, 1932, J. B. Wolters Ed., Groningen.



The most notable advance towards that goal was made by Bravais. The Bravais Principle states (with certain restrictions) that the faces which occur on a crystal are parallel to the planes with maximum reticular density in a *properly chosen lattice*, and that the denser the net plane, the more important the corresponding face. It is obvious that the lattice in question cannot be known in absolute magnitude since it is determined by reflection goniometry only. Given three axial directions (for instance, by their interaxial angles,  $\alpha, \beta, \gamma$ ) and the axial ratios  $a:b:c$ , a lattice can be built, in which  $b$  is taken as an arbitrary unit of length. Such a lattice is therefore completely determined as soon as the three pinacoids and the unit form (or parametral form) have been selected (*it is not necessary to know which is which*).

Because Bravais arrived at this principle by means of speculations as to the internal structure of the crystal, the truth of his statement was long in question. Only since 1907, when G. Friedel<sup>6</sup> demonstrated in a convincing way that this principle is purely a law of observation, valid independently of any structural hypothesis, has the principle received general acceptance. It is now known as the Law of Bravais and, although often considered a distinct law, it is nothing else than a more complete and more precise statement of Haüy's law of rationality. In its complete form, the latter might appropriately be called the Law of Haüy-Bravais.

The law of maximum reticular densities leads to the determination of a lattice, the Haüy-Bravais lattice,<sup>7</sup> which is, for most substances, uniquely determined. In contrast to this, the requirement of *simple indices*, or even Barker's more restrictive principle of *simplest indices*, does not lead to an unambiguous choice of lattice. Hence the lack of agreement prevailing today as to the crystallographic constants of many species.

The various steps of the method will now be briefly outlined.<sup>8</sup>

<sup>6</sup> His original investigation (*Bull. Soc. franç. Min.*, vol. 30, p. 326, 1907) is summarized in his text-book, G. Friedel, *Leçons de Cristallographie*, 1926.

<sup>7</sup> Friedel calls it the Bravais lattice. Donnay and Mélon proposed to call it Haüy-Bravais lattice since the term "Bravais lattices" is used with another meaning (the 14 Bravais lattices). The new term stresses the fact that the lattice in question is obtained by giving the law of Haüy-Bravais a proper expression.

<sup>8</sup> A complete example of the determination of the Haüy-Bravais lattice in the case of a triclinic crystal was recently published in this Journal. To our knowledge, it is the first article in English on the subject. Donnay and Mélon, *Am. Mineral.*, vol. 18, pp. 225-247, 1933.

1. PROVISIONAL LATTICE. A provisional set of axial elements is determined, from the measurements. No special attention need be given to the simplicity of indices or any other consideration at the outset. These axial elements define a space-lattice, that is, the assemblage of all the points at the corners of contiguous parallelepipeds, all identical with the cell built on the three axial directions and the three unit-lengths  $\tilde{a}$ ,  $\tilde{b}$ ,  $\tilde{c}$ . This lattice is one of the seven primary lattices (of course it is not defined in absolute magnitudes).

2. DETERMINATION OF THE HAÜY-BRAVAIS LATTICE. Observe the order of importance of the forms present on the crystals studied. List these forms according to decreasing importances and number them accordingly: 1, 2, 3, . . . The importance of a form is in proportion to the frequency of occurrence of the form and the size of its faces; the fact that a crystal form coincides with a cleavage form is also an indication of its importance. In terms of *rate of growth*, faces with a slow rate of growth are the most important since they control the outline and general appearance of the crystal; the importance is thus inversely proportional to the rate of growth. The listing of the faces in the order of their importance may present difficulties when the crystals show widely different habits. This investigation is then statistical in scope. Next compute the reticular densities of the denser net planes in the provisional lattice. The reticular density of a net plane is defined as the number of lattice points per unit of area; it is proportional to the *spacing* (or interplanar distance) of parallel net planes; it is inversely proportional to the *reticular area* which is the area of the smallest two-dimensional cell (parallelogram) in the net plane. For the isometric system the reticular area,  $S$ , of a plane ( $hkl$ ) is given by the formula

$$S^2 = a^4(h^2 + k^2 + l^2)$$

where  $a$  denotes the length of the edge of the unit-cell (the geometrical crystallographer takes  $a=1$  since he has no way of ascertaining its absolute value). List the net planes in the order of their decreasing reticular densities.

Compare the two lists as to agreement. The known forms should occur at the beginning of the theoretical list and they should appear in the order of their decreasing importances if the lattice is well chosen. Usually this will not be the case.



By trial, modify the first lattice until a correct expression of the Law of Bravais is reached.

These modifications must of course lead to a new lattice isogonal with the first one. That is to say, the angles between lattice planes must always be equal to the corresponding interfacial angles of the crystal. This condition will be fulfilled if the modifications consist of systematic addition or subtraction of lattice points (such as halving or doubling a parameter, for instance). Now since the size of the lattice is immaterial for the present purpose, it is clear that any modification obtained by leaving out points can equally well be reached by adding (other) points (for example, doubling the  $c$  parameter leads to the same result as halving both the  $a$  and the  $b$  parameters). Hence the only modifications to be considered are those brought about by a systematic *addition* of points. The coordinate axes chosen for the provisional lattice may be retained, since the assemblage of points, not the way they are defined, is the important thing. The modifications to be tried are then: to center the provisional cell (body-centering) or to center one, two, or all three of its faces (face-centering). These modifications may be tried in succession, singly or jointly, until the list of lattice planes prepared according to decreasing reticular densities agrees with the list of observed importances of the known crystal faces.

When a lattice has been found to give a satisfactory expression to the Law of Bravais, it is chosen as the morphological lattice. Notice that this Haüy-Bravais lattice is one of the 14 Bravais lattices, that one which best expresses the morphology of the crystal to be described. It should be borne in mind that these morphological lattices (*geometrical pictures* only) are "relative" or "elastic" lattices, in contradistinction to the structural lattice (a *physical reality*) determined in absolute magnitudes by  $x$ -ray investigation. The primitive translations of the "elastic" lattice are designated by  $a$ ,  $b$ ,  $c$ ; those of the "absolute" lattice are represented by  $a_0$ ,  $b_0$ ,  $c_0$ .

Although at the present time the Haüy-Bravais lattice probably affords the best means of accounting for the presence and relative importance of the observed faces of a crystal, it is obvious that, nevertheless, it is an imperfect tool. Let it suffice to recall one of its limitations: faces which are symmetrical (equivalent, or similar) as far as their directions are concerned, may be dissimilar from the physical point of view. Example: the faces of the two comple-

mentary tetrahedra in the tetartoidal class (tetartohedral class of the isometric system), from the viewpoint of their directions only, are all equivalent and constitute an octahedron. In other words, their reticular densities, as computed from the morphological lattice, will be the same. According to the Law of Bravais, they should be equally important (equally developed, equally frequent, and have the same rate of growth), but it is well known that two such physically different complementary forms do not always occur together or have the same development. In all likelihood this is due to the influence of the symmetry of the *motif* (= symmetry of the *crystal*), which in such cases is lower than that of the lattice itself. Friedel has shown, however, that the influence of the *motif* is much smaller than that of the *lattice*: he points out that in many cases complementary forms of high reticular density do occur together and that one of the complementary forms is missing only when the density of the form is sufficiently low.

There is a small chance of finding more than one lattice giving the Law of Bravais a correct expression. In such cases where the Haüy-Bravais lattice is not uniquely determined by the above method, Friedel's "Law of Mean Indices"<sup>9</sup> provides an additional method of obtaining the desired lattice. The scope of this paper permits only brief mention of this remarkable law.

\* 3. CHOICE OF AXIAL ELEMENTS TO DEFINE THE HAÜY-BRAVAIS LATTICE. The Haüy-Bravais lattice can now be defined (expressed) in a great many different ways. The axes of coordinates may be any three non-coplanar lattice-rows, so that the choice of the axial directions is equivalent to the choice of a *cell* in the lattice. Then, after a certain cell has been chosen, the three axes remain to be directed (given a positive sign). We will consider suggestions as to such choices.

(A) *Choice of the cell used to define the Haüy-Bravais lattice.* Although the lattice is only the assemblage of points in space, it is convenient to consider it as being built up of stacked parallelepipeds or cells. The cell may have an infinite number of shapes. Any four non-coplanar lattice-points may serve to define a cell. When the parallelepiped does not contain any other lattice-point than its eight corner-points, the cell is said to be a *simple cell* (one point per cell). When there is more than one point per cell, the cell is called a *multiple cell*.

<sup>9</sup> Friedel, G., *Leçons de Cristallographie*, 1926, p. 134.



The choice of the cell may be guided by the following considerations:

(a) Simplicity of indices. A cell leading to simple indices should obviously be given preference for the sake of convenience.

(b) Pseudo-symmetry. If the crystal exhibits a *well-marked* pseudo-symmetry, this fact should be expressed by the choice of the cell, even at some expense of simplicity of indices. A classic example is that of *epidote*, monoclinic, pseudo-orthorhombic ( $\beta = 90^\circ 34'$ ), which was brought out by G. Friedel.<sup>10</sup> There is room for personal divergences of opinion, however, as to what should be considered "well-marked pseudo-symmetry." Some crystals have been called pseudo-symmetrical, which hardly deserve such description. The point should not be stretched and pseudo-symmetries are not to be found at all cost! When pseudo-symmetry is striking enough to be noticed on the crystals, then it seems appropriate to express the fact by the choice of a cell showing this pseudo-symmetry.

(c) Smallest translations. It has been suggested that the cell be chosen with the smallest three primitive translations. This criterion has the advantage of leading to a unique solution. It should always be used unless there are good reasons to adopt another cell (see (a) and (b)).

(B) *Orientation of the axes.* The cell having been chosen, it remains to name and direct the axes. There are 48 alternatives if no restriction be imposed on the type of system of coordinates. Crystallographers have used both the left-handed system (Fedorov, Mallard) and the right-handed system. The latter is almost universally adopted at the present time. With it we still face 24 possibilities. They can be visualized if the origin of coordinates be carried successively to the eight corners of the cell and, in each case, the edges of the cell taken for the positive directions of the axes. At each corner the axes may be called either  $a, b, c$ ; or  $b, c, a$ ; or  $c, a, b$ , since the right-handed character of the system of coordinates is not altered by these three cyclic permutations.

The first suggestion to direct the choice is to express the habit by placing the *main zone* vertically. The main zone is either parallel to the direction of elongation (in prismatic or acicular crystals) or perpendicular to the plane of flattening (tabular habit). The choice of the  $c$ -axis at each corner of the cell determines the other two axes

<sup>10</sup> *Leçons de Cristallographie*, 1926, p. 140.

since the system must be right-handed, so that the number of alternatives is now reduced to eight. This suggestion is apparently the only one that can be made in order to express habit. The others will be mere arbitrary conventions.

Considering the most general case (triclinic system), and using only proposals already made by various crystallographers, we suggest that  $a$  be taken smaller than  $b$ , that the  $a$ -axis slope forward, and that the  $b$ -axis slope to the right; this leaves only one alternative.

For monoclinic crystals, the direction of the  $b$ -axis is fixed by symmetry. There exists no convention as to the naming of the other two axes. Following the same principle as in the triclinic system, we may place the direction of elongation vertically. A greater elongation along the  $c$ -axis than along the  $a$ -axis corresponds to a  $c$ -parameter smaller than the  $a$ -parameter, as the *linear density* must be higher for the  $c$ -axis. Finally, the  $a$ -axis should slope forward.

In the orthorhombic system the first criterion is the same as in the triclinic system, that is to say, the main zone is placed vertically. The only other necessary condition is the age-old convention:  $a < b$ .

4. MORPHOLOGICAL SIGNIFICANCE OF THE ADOPTED AXIAL ELEMENTS. To what extent does such a set of axial elements throw light on the morphology of the crystal?

We may distinguish the following points to be considered:

(A) The *crystal forms observed* (all of which need not be found on all the crystals of the same crystalline species).

(B) The *form combinations* observed, irrespective of differential form development. Example: the combination "cube-dodecahedron" in the isometric system.

(C) Unequal development of the forms observed on one combination. Examples: cube dominant modified by dodecahedron; cube-dodecahedron about equally important; dodecahedron with small cubic truncations, etc.

(D) Unequal development of the faces of the same form (malformation, German *Verzerrung*, French *difféormité*).

The word *habit* (German *Tracht*, *Habitus*; French *facies*) has been used with different meanings.<sup>11</sup> It practically covers the last three points mentioned.

The Haüy-Bravais lattice to which the crystal is referred enables one to forecast what the principal forms will be and their relative

<sup>11</sup> Cf. Chudoba, *Centralblatt für Min.*, 1933, Abt. A, p. 99.



importances (they should be among the first in the list of net planes arranged according to decreasing reticular densities). This yields much information on the points, (A), (B), (C).

The cell chosen to define the Haüy-Bravais lattice brings out pseudo-symmetry if it be present.

The direction of the  $c$ -axis will also give useful information on the third point. Malformation cannot be expressed by the axial elements.

All the other conventions necessary to determine uniquely the cell orientation have no value insofar as morphological characterization is concerned. They are only useful in standardizing the description of crystals.

5. REMARKS ON THE DETERMINATION OF RETICULAR DENSITIES. The difficulty in determining the proper set of axial elements for accurate morphological description lies in the determination of reticular densities for a fairly large number of planes. A few hints may be given as to how to proceed.

If a calculating machine is available, compute the square of the reticular area (instead of the reticular density), which is given by a formula of analytical geometry.<sup>12</sup> Use of tables of natural values of trigonometric functions<sup>13</sup> simplifies the procedure. The accuracy of the method is here dependent on the accuracy of the geometric measurements of the crystal.

Graphic methods have been devised for the determination of reticular densities with an accuracy sufficient for the purpose in most cases. A review of these methods is given by Terpstra and van Weerden<sup>14</sup> who generalized the theorem on which these methods are based.

Other methods can be devised to suit particular problems. In all crystal systems except the triclinic a semi-graphical method has been found satisfactory and rapid. The formula giving the value of  $S_{(hkl)}^2$ , where  $S_{(hkl)}$  is the reticular area of the net plane  $(hkl)$  is of the form:

$$S^2 = h^2 b^2 c^2 + k^2 c^2 a^2 + l^2 a^2 b^2$$

in the orthorhombic system. The values of  $b^2 c^2$ ,  $c^2 a^2$ ,  $a^2 b^2$ , are computed. Three rulers are then prepared on stiff drawing paper, graduated for the different values of  $h^2 b^2 c^2$ ,  $k^2 c^2 a^2$ ,  $l^2 a^2 b^2$ , respectively.

<sup>12</sup> This formula may be found in Friedel, *op. cit.*, p. 235.

<sup>13</sup> Ives, Howard Chapin, Natural trigonometric functions to seven decimal places for every ten seconds of arc. John Wiley & Sons, New York, 1931.

<sup>14</sup> Graphical methods for the determination of reticular densities and lattice parameters (to appear in *Am. Mineral.*).

The first one, for example, shows the divisions 0,  $b^2c^2$ ,  $4b^2c^2$ , . . . numbered 0, 1, 2, . . . according to the value of  $h$ . A large sheet of millimeter paper is used for plotting the values of  $S^2$  for the various lattice planes. The addition is carried on graphically by means of the three rulers. The result is a sheet covered with points (one for each crystal form). The abscissae of the points are proportional to the square of the reticular area; they are therefore arranged in the order of their decreasing reticular densities.

6. REMARKS ON THE FEDOROV METHOD. As stated in the section on determinative crystallography, Fedorov's main purpose was to find the "correct orientation." His work is little known for the reason that his publication (*Das Krystallreich*), although written in German, is not explicit enough. As a matter of fact, it is so concise that Boldyrev<sup>15</sup> found it necessary to publish explanatory comments on it. Unfortunately, these are in Russian, and are hence, as yet, of little use to most crystallographers outside of Russia.

A few points may be mentioned as to the nature of the Fedorov method. Use is made of the Bravais Principle and it is even attempted to make its application quantitative. The "correctness" of the orientation is measured by a quantity,  $W$ , which is, among other things, a function of the ratio  $R/J$ , in which  $R$  is the sum of the squares of the reticular densities of the  $n$  observed forms, and  $J$  the sum of the squares of the reticular densities of the  $n$  theoretical forms with the highest reticular densities. The closer the quantity  $W$  is to one, the better the corresponding orientation. In spite of this apparently quantitative character, the Fedorov method disregards an important criterion—the order of importance of the observed forms. It only discriminates between the presence or the absence of a form, hence the Law of Bravais is not used to full advantage. Moreover, the quantitative "measure" of the correctness of the orientation may be judged somewhat artificial, having, at any rate, less physical reality than the order of importance of the observed forms, qualitative as the latter criterion may be.

### III. THE STRUCTURAL DESCRIPTION OF CRYSTALS AND THE RÖNTGENOGRAPHIC DETERMINATIVE METHOD

1. STRUCTURAL ANALYSIS. The use of present-day  $x$ -ray diffraction apparatus makes it possible simply and rigorously to determine the structural space lattice of a crystal—one of the 14 Bravais lattices—with absolute magnitudes of the lattice di-

<sup>15</sup> Boldyrev, A. K., *Kommentarii k rabote E. S. Fedorova, Das Krystallreich, Acad. Leningrad, 1926.*



mensions. The first determinations of structural space lattices with absolute magnitudes were carried out in 1913 by the Braggs<sup>16</sup> and concerned a series of alkali halides studied with the aid of Laue photographs and ionization spectrometer measurements. Previously neither the absolute wave-lengths of x-rays nor the absolute cell dimensions of any crystal were known. By comparison of the positions and intensities of the x-ray diffraction spectra from successive members of the isomorphous series and with the aid of plausible assumptions W. L. Bragg was able to deduce the atomic arrangements in these compounds and to calculate the absolute spacings of their lattices. Bragg pointed out that it was not possible to prove the conclusions rigorously with the data then available, but he showed that any other interpretation was very improbable. Subsequent determinations of the absolute wave-lengths of x-rays by methods independent of knowledge of crystal structures (such as diffraction by artificially ruled gratings) has confirmed Bragg's conclusions as to the atomic arrangement and lattice dimensions in the alkali halides. The first complete determination of the lattice of a triclinic crystal by purely röntgenographic methods appears to have been accomplished by Schneider<sup>17</sup> with the use of the Weissenberg goniometer, the substance being anhydrous mesotartaric acid.

At present the most convenient way of finding the structural space lattice of a monoclinic or triclinic crystal is by the use of the Weissenberg goniometer<sup>18</sup> and the graphical construction devised by Schneider.<sup>19</sup> This method leads to a unique and rigorous determination of the reciprocal lattice and hence of the structural space lattice, and is very straightforward in its practical application. It has been restated in English in this Journal by one of the present writers<sup>20</sup> and need not be reviewed here. With crystals belonging to systems of higher symmetry it is of course readily pos-

<sup>16</sup> *Proc. Roy. Soc. London*, **89A**, pp. 248-277, 1913.

<sup>17</sup> *Zeit. f. Krist.*, vol. **69**, p. 49, 1928.

<sup>18</sup> Weissenberg, K., *Zeit. f. Physik*, vol. **23**, p. 229, 1924.

<sup>19</sup> *Zeit. f. Krist.*, vol. **69**, p. 41, 1928.

<sup>20</sup> Tunell, G., *Am. Mineral.*, vol. **18**, p. 276, 1933. (Note. In this paper Tunell did not follow the terminology of Bernal in one particular. Bernal reserves the phrase "circle of reflection" for circular sections of the cone of reflection, whereas Tunell applied this phrase to circular sections of the sphere of reflection, which Bernal refers to simply as "circles of section." Tunell's different usage was unintentional, and we shall adhere to the usage of Bernal hereafter, although Bernal's terminology in this particular is not entirely felicitous.)

sible to work out the structural lattice by means of rotation-oscillation photographs and in some cases from powder or Laue photographs.

When the structural lattice has been determined the choice of a unit cell remains to be made, since the same lattice can be built up by means of different unit cells. In structural analyses the unit cell is conveniently so chosen and so orientated as to permit the direct application of tables of equivalent positions and röntgenographic extinctions such as Wyckoff's "The analytical expression of the results of the theory of space groups,"<sup>21</sup> Niggli's "Geometrische Kristallographie des Diskontinuums," Astbury and Yardley's "Tabulated data for the examination of the 230 space-groups by homogeneous X-rays,"<sup>22</sup> and K. Herrmann's "Röntgenographische Auslöschungstabellen."<sup>23</sup> In these tables particular locations and orientations of the symmetry elements are presupposed and the actual crystal to be compared with the tables must be set up so that its own symmetry elements occupy analogous locations in the unit cell. The choice of the unit cell in structural analysis is thus mainly governed by the röntgenographic extinctions. It is not necessarily the "smallest repeat" or *true period*. The unit cell may be a multiple cell, the smallest multiple cell which possesses the whole symmetry of the lattice.

2. RÖNTGENOGRAPHIC IDENTIFICATION. Although little work has been done as yet along this line, it seems probable that determinative tables based on structural characters as revealed by x-rays will be prepared in the future. In the compilation of such determinative tables of absolute unit cell dimensions arbitrary rules must be specified for the selection and naming of the axes. In the triclinic system the unit cell must be chosen from an infinite number of possible cells all having the same volume; we propose that for this purpose the three planes be selected as pinacoids the spacings of which are the largest of any three non-tautozonal planes in the crystal.<sup>24</sup> In the monoclinic system the *b*-axis is fixed in direction and unit length; in the zone parallel to the *b*-axis the two planes of greatest and second greatest spacing may be chosen as

<sup>21</sup> Carnegie Institution of Washington, Publication No. 318, Second Edition, 1930.

<sup>22</sup> *Phil. Trans. Roy. Soc. London*, vol. 224A, p. 221, 1924.

<sup>23</sup> *Zeit. f. Krist.*, vol. 68, p. 288, 1928.

<sup>24</sup> This suggestion is analogous to the Law of Bravais in that it emphasizes the fundamental character of the planes of greatest spacing or reticular density. The Law of Bravais is, however, a rule concerning the surface form development of the crystal, originally formulated from structural hypotheses, it is true, but now di-



pinacoids. For the determinative tables it is most convenient in the isometric system to take as the unit cell a cube, no matter which of the three cubic lattices is to be built up, notwithstanding the fact that a smaller rhombohedral unit cell could be used for face-centered and body-centered isometric lattices. In the triclinic, monoclinic, and orthorhombic systems arbitrary rules must be adopted for the naming and directing of the three crystallographic axes after the three pinacoidal planes have been selected. With such rules a given compound will always be described in the same way and will not require more than one entry in a table.

When determinative tables of absolute unit cell dimensions have been assembled it will still be true that a determinative investigation can be carried out more quickly with the reflection goniometer than with the *x*-ray goniometer in most cases. However, when dealing with crystals without measurable faces one cannot apply the reflection goniometer at all whereas the *x*-ray goniometer may still be used even if the anhedron be a twin.

The rules for selecting and orientating the unit cell for determinative purposes will not always lead to the same unit cell and orientation as that utilized in the tables of equivalent positions; the reason for this is that the positions of the symmetry elements are not in general determined by the lengths of the edges of a unit cell or the angles between the edges. It is not necessary, in order to build up and use determinative tables on the principles outlined, to know the positions of all the symmetry elements in the unit cell, and it seems a useless complication of determinative technique to make it depend on such knowledge. In *x*-ray analysis as well as in studies of the external form development we must be prepared in some cases to use different orientations of the same crystal, according as our purpose is the determination of the substance (crystallochemical analysis) or the establishment of its atomic arrangement.

At the present time the construction of determinative tables of absolute unit cell dimensions has not proceeded as far as that of tables of relative dimensions by the method of Barker; nevertheless, extensive tables of absolute unit cell dimensions of isometric chemical elements, compounds, and alloys have been prepared by Knaggs, Karlik, and Elam,<sup>25</sup> and will serve a useful purpose just

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vorced from them. It is obvious that in some cases the Haüy-Bravais lattice may not be geometrically similar to the absolute unit cell determined by the rule suggested for use in compilation and application of determinative tables.

<sup>25</sup> Knaggs, I. E., Karlik, B., and Elam, C. F., *Tables of Cubic Crystal Structure of Elements and Compounds with a Section on Alloys*, London, 1932.

where the tables of relative dimensions are of no avail (isometric system).<sup>26</sup>

A few words may be added concerning the relative precision of the x-ray and reflection goniometer measurements in present practice. In the x-ray method the instrumental error varies greatly with different arrangements of apparatus. The measurements may be made with extreme precision (to seconds of arc) by means of the double crystal spectrometer; on the other hand a rough estimation of the dimensions of the unit cell can be obtained from Laue photographs, although, as Wyckoff states, it is much more satisfactory to secure them from single-face spectra. Measurements with the Weissenberg goniometer are of intermediate accuracy with an error of  $\pm \frac{1}{2}^\circ$  down to as little as  $\pm \frac{1}{4}^\circ$  in favorable cases. In reflection goniometry the precision depends chiefly on the perfection of the crystal faces and with good crystals it is usually a matter of a few minutes, in exceptional cases as little as 1' or even  $\frac{1}{2}'$ .

#### IV. RELATION BETWEEN THE MORPHOLOGICAL AND THE STRUCTURAL SPACE-LATTICES

Inasmuch as the rules leading to the choice of determinative crystal constants (Barker or röntgenographic) are arbitrary conventions, it is not surprising that the "determinative lattices" arrived at by such methods should be at variance with the other two kinds of space-lattice, morphological and structural. But since the latter are the expression of *observed facts* concerning the crystal constitution they might *a priori* be expected to be one and the same thing. It is a baffling fact that the *Häüy-Bravais lattice*, as determined by the morphology of the crystal, may or may not be the same as the *Bravais lattice* resulting from the structural investigation. Two examples will illustrate this observation.

1. EXAMPLE OF AGREEMENT: Pseudobrookite. The axial elements of pseudobrookite have recently been determined by Charles Palache,<sup>27</sup> who gives the following values as the mean of his own and other reliable determinations:

$$a:b:c = 0.9777:1:0.3727.$$

<sup>26</sup> A powder photograph is characteristic of a substance. Hence a complete collection of powder pictures might serve for determinative purposes. It is recognized that this procedure is very serviceable as a means of checking an identification, but it is rather obvious that the comparison of powder photographs is inherently inconvenient as a method of determining an unknown substance that may be any one of thousands.

<sup>27</sup> *Am. Mineral.*, vol. 19, pp. 14-20, 1934.



Pseudobrookite, being orthorhombic, can be referred to four different types of lattice:

- 1—Simple orthorhombic lattice or rectangular hexahedral mode;
- 2—Body-centered orthorhombic lattice or rectangular octahedral mode;
- 3—All-face-centered orthorhombic lattice or rhombic octahedral mode;
- 4—One-face-centered lattice or rhombic hexahedral mode. Some authors always place the centered face horizontal, hence the other name of the mode: base-centered orthorhombic lattice.

In the simple orthorhombic lattice, the square of the reticular area,  $S$ , for any plane ( $hkl$ ) is given by the formula:

$$S_{(hkl)}^2 = a^2 b^2 c^2 \left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right),$$

which may be written in the more convenient form:

$$S_{(hkl)}^2 = a^2 b^2 (h^2 m' + k^2 m'' + l^2) \quad (A)$$

where  $m' = c^2/a^2$ ,  $m'' = c^2/b^2$ .

The following values are found for pseudobrookite:

$$m' = 0.1453, \quad m'' = 0.1389.$$

The formula (A) can easily be computed graphically or semi-graphically.

A list of planes is obtained (for the simple lattice) arranged according to decreasing reticular densities or, what is equivalent, increasing  $S^2$ , since  $S$  is inversely proportional to the reticular density. Similar lists can be obtained for the other modes of the orthorhombic lattice by applying the following rules:

1. For the body-centered lattice, multiply by 4 the  $S^2$  of all planes ( $hkl$ ) for which the sum of the indices ( $h+k+l$ ) is odd.
2. For the all-face-centered lattice, multiply the  $S^2$  by 4 for all planes ( $hkl$ ) whose indices are *not all odd*.
3. For the one-face-centered lattice, multiply the  $S^2$  by 4,
  - (a) if the cell is centered on  $\{100\}$ , for all planes ( $hkl$ ) when the sum ( $k+l$ ) is odd;
  - (b) if the cell is centered on  $\{010\}$ , for all planes ( $hkl$ ) when the sum ( $l+h$ ) is odd;
  - (c) if the cell is centered on  $\{001\}$ , for all planes ( $hkl$ ) when the sum ( $h+k$ ) is odd.

These rules yield lists of planes in the proper order of decreasing reticular densities, although they only give values of  $S^2$  which are proportional to the true values.

The results of our semi-graphic determinations are shown in Table I.

TABLE I

LIST OF PLANES ACCORDING TO DECREASING RETICULAR DENSITIES IN VARIOUS MODES OF LATTICE FOR PSEUDOBROOKITE

Simple	Body-centered	{100}-centered	{010}-centered
<i>b</i> 010*	<i>m</i> 110*	<i>a</i> 100*	<i>b</i> 010*
<i>a</i> 100*	<i>b</i> 010*	<i>b</i> 010*	<i>a</i> 100*
<i>m</i> 110*	<i>a</i> 100*	<i>n</i> 120*	$\mu$ 210*
<i>n</i> 120*	011	$\left\{ \begin{array}{l} m \\ m \end{array} \right\}$ 110*	$\left\{ \begin{array}{l} m \\ e \end{array} \right\}$ 110*
$\mu$ 210*	<i>e</i> 101*	011	<i>e</i> 101*
001	130	<i>q</i> 111*	<i>q</i> 111*
011	310	211	<i>s</i> 121*
<i>e</i> 101*	<i>s</i> 121*	320	230
<i>q</i> 111*	211	<i>y</i> 031*	<i>l</i> 301*
130	<i>y</i> 031*	140	<i>p</i> 131*
310	<i>l</i> 301*	<i>p</i> 131*	410
021	310	231	<i>n</i> 120*
201	<i>n</i> 120*	$\mu$ 210*	321
<i>s</i> 121*	231	411	141
211	$\mu$ 210*	<i>h</i> 340*	331
230	141	331	430
320	411	001	001
...	...	...	...
The above forms are followed, but not consecutively, by:			
<i>y</i> 031*	<i>q</i> 111*	<i>e</i> 101*	<i>y</i> 031*
<i>l</i> 301*	<i>p</i> 131*	<i>s</i> 121*	<i>h</i> 340*
<i>p</i> 131*	<i>h</i> 340*	<i>l</i> 301*	
<i>h</i> 340*			

N.B. For every observed form, marked by an asterisk, the letter preceding the Miller symbol is that used by Palache (op. cit.).

A scrutiny of the various descriptions of pseudobrookite from 8 different localities and of artificially prepared crystals leads to the following conclusions as to the observed importance of forms: 1—*b*{010}, the only cleavage, a very frequent form although not always present.

2—*a*{100} and 3— $\mu$ {210}, both universally present, the two largest forms, *a* being larger than  $\mu$ , tabular on *a*.

4—5—*m*{110}, *e*{101}, listed as equally important: *e* is universally present whereas *m* is only fairly frequent; on the other hand, *m* belongs to the main zone thus making up in length

what it lacks in width so that it can compare in size with the more equant  $e$ .

6— $q\{111\}$ , it is still possible to recognize  $q$  as the next important form: rather frequent and probably larger than any of the other subordinate forms.

7 to 11— $s\{121\}$ ,  $l\{301\}$ ,  $p\{131\}$ ,  $n\{120\}$ ,  $y\{031\}$ , all uncommon, minor forms, hard to differentiate.

12— $h\{340\}$ , undoubtedly the least important, found in one locality only.

Comparison of the list of observed form importances with the theoretical lists in Table I clearly shows that the only mode which fits the facts is the lattice centered on  $\{010\}$ . The first plane in that list is the only cleavage of the mineral,  $b\{010\}$ , the next four are the four most important forms:  $a\{100\}$ ,  $\mu\{210\}$ ,  $m\{110\}$ ,  $e\{101\}$  in their correct order;<sup>28</sup> the first four planes belong to the vertical zone, highly dominant since the crystals are prismatic to acicular in that direction; the last observed plane,  $h\{340\}$ , is the least important. Out of 12 forms observed, 10 appear among the first in the list: they are the first ten except for two gaps: one after the 7th form, and one after the 9th. No lattice mode except the lattice centered on  $\{010\}$  shows as many as 10 observed forms among the first 12 in the list. The other modes have only 7. Gaps occur in the other modes, much more frequently and earlier in the list than in the  $\{010\}$ -centered lattice. The other possible lattice modes are not given here. It can be seen at a glance that the modifications in the order of forms brought about by centering all the faces of the cell will make the theoretical list depart even more from the experimental list. The same is true of the other alternatives.

The translation group determined by L. Pauling<sup>29</sup> is  $\Gamma_0'$ , the same as the one found here by morphological methods. In this case, the structural lattice and the morphological lattice are identical, with the restriction of course that the morphological lattice is not determined with absolute values of the parameters but only ratios thereof. In this sense, the morphological lattice of pseudobrookite is strictly proportional to its structural lattice. This is not true

<sup>28</sup> Prof. Charles Palache pointed out to us that the form  $e\{101\}$  comes rather far down in the theoretical list. We found that the reticular densities of  $m\{110\}$  and  $e\{101\}$  are proportional to 0.938 and 0.936 respectively, and it is obvious that a difference of the order of two-tenths of one per cent is here meaningless. The theory thus brings out the observed "nearly equal importance" of  $m$  and  $e$ .

<sup>29</sup> *Zeit. f. Krist.*, vol. **73**, p. 97, 1930.



of all substances, however. In numerous cases the two lattices are not the same.

2. EXAMPLE OF DISAGREEMENT: Calcite. The most spectacular example of divergence between the two lattices is found in calcite, which was studied by G. Friedel (see *Leçons de Cristallographie*, pp. 142 et seq.). He has shown that the true morphological lattice is rhombohedral with the cleavage rhombohedron as a unit cell

TABLE II

<i>Structural lattice of calcite</i> Unit cell is $e^3 \{11\bar{3}\} \{04\bar{4}1\}$ , the true period			<i>Morphological lattice of calcite</i> Unit cell is $p \{100\} \{10\bar{1}1\}$ , the cleav- age rhombohedron		
$a^1$	$\{111\}$	$\{0001\}^{**}$	$p$	$\{100\}$	$\{10\bar{1}1\}^{**}$
$e^3$	$\{11\bar{3}\}$	$\{04\bar{4}1\}^*$	$d^1$	$\{10\bar{1}\}$	$\{1120\}^*$
$e^1$	$\{11\bar{1}\}$	$\{0221\}^{**}$	$e^1$	$\{11\bar{1}\}$	$\{02\bar{2}1\}^{**}$
$p$	$\{100\}$	$\{10\bar{1}1\}^{**}$	$b^1$	$\{110\}$	$\{01\bar{1}2\}^{**}$
$e^{1/3}$	$\{33\bar{1}\}$	$\{0445\}^*$	$e^2$	$\{112\}$	$\{0110\}^{**}$
$d^1$	$\{10\bar{1}\}$	$\{1120\}^*$	$d^2$	$\{20\bar{1}\}$	$\{2131\}^{**}$
$\alpha$	$\{513\}$	$\{4483\}^*$	$a^1$	$\{111\}$	$\{0001\}^{**}$
$e^{5/3}$	$\{335\}$	$\{0881\}^*$	$e_2$	$\{21\bar{1}\}$	$\{1232\}^*$
$a^5$	$\{511\}$	$\{4047\}^{**}$	$b^2$	$\{210\}$	$\{1123\}^*$
$b^1$	$\{110\}$	$\{01\bar{1}2\}^{**}$	$e_{1/2}$	$\{212\}$	$\{1341\}^*$
$e_3$	$\{31\bar{1}\}$	$\{2243\}^*$	$e^3$	$\{11\bar{3}\}$	$\{04\bar{4}1\}^*$
$e^7$	$\{117\}$	$\{0885\}$	$d^3$	$\{30\bar{1}\}$	$\{3143\}^*$
$\gamma$	$\{517\}$	$\{4.8.12.1\}^*$	$a^2$	$\{211\}$	$\{10\bar{1}4\}^*$
$e^{3/5}$	$\{553\}$	$\{0887\}^*$	$e^{1/2}$	$\{22\bar{1}\}$	$\{0111\}^*$
$e_{1/3}$	$\{31\bar{3}\}$	$\{24\bar{6}1\}^*$	$d^{3/2}$	$\{30\bar{2}\}$	$\{3251\}^*$
$a^3$	$\{311\}$	$\{2025\}^*$		$\{213\}$	$\{1450\}$
$d^2$	$\{20\bar{1}\}$	$\{2131\}^{**}$	$e_3$	$\{31\bar{1}\}$	$\{2243\}^*$
	$\{73\bar{1}\}$	$\{4489\}$		$\{312\}$	$\{2352\}^*$
$a^{1/5}$	$\{551\}$	$\{0.4.\bar{4}.11\}$	$b^3$	$\{310\}$	$\{2134\}^*$
$e^2$	$\{112\}$	$\{0110\}^{**}$	$e^{3/2}$	$\{223\}$	$\{0551\}^*$
.....			.....		

N.B. Every observed form is given in the Lévy form-notation as well as by its Miller indices.

$p\{100\}\{10\bar{1}1\}$ . The structural period, however, is a much more elongated rhombohedron:  $e^3\{11\bar{3}\}\{04\bar{4}1\}$ . Friedel refers calcite to a set of three coordinate axes (left-handed system), the lower terminal edges of the cleavage rhombohedron. We reproduce here two of his lists of planes according to decreasing densities with the Bravais-Miller four-index symbols next to Friedel's symbols. We

do this only in order to facilitate the reading of these lists by American crystallographers, since the four-index symbols are still widely used in this country for the five classes of the rhombohedral subsystem, even when the lattice is known to be rhombohedral. We believe that, in these five classes, it would be better to use the 3-index notation when the lattice is rhombohedral, reserving the 4-index symbols for crystals with hexagonal lattices.

Friedel's lists are given in Table II.

In these lists, the forms observed on calcite crystals are marked by asterisks; the six most important known forms are indicated by two asterisks, the remainder by one. A glance at the two lists will convince the reader that the second lattice accounts for the relative importance of the known forms much better than the first one. With one exception<sup>30</sup> (for, as Friedel himself points out, "reticular densities do not explain everything"!), the six main forms are at the top of the list; moreover, the cleavage forms  $p$ , and  $b^1$  and  $e^1$  are certainly more important than the next three in the list, and  $a^1$  is the least important morphologically among the six dominant forms. Friedel also considers another lattice, based on the unit cell  $e^1\{11\bar{1}\}\{0221\}$ . Incidentally this is the true structural lattice of the high-temperature form of  $\text{NaNO}_3$ , which has the calcite structure, but whose structural period along the  $c$ -axis nevertheless is only half that of calcite (due to a rotation of the  $\text{NO}_3$ -ions with consequent structural equality of all the  $\text{NO}_3$ -ions). This lattice would account for the morphological observations on calcite better than that based on  $e^3\{11\bar{3}\}\{0441\}$  but it is far from being as satisfactory as the lattice based on the cleavage rhombohedron as unit cell. Friedel remarks that the latter cell would be the period if no distinction were made between the Ca-ions and the  $\text{CO}_3$ -ions (Fig. 1).

He also makes a similar observation in the case of halite (sodium chloride). The morphological lattice is here simple cubic whereas the structural lattice is face-centered. If the difference between the Na- and the Cl-ions be disregarded, however, all ions being then

<sup>30</sup> This apparent exception can be explained by an observation due to Friedel, G. (*Bull. Soc. fr. Min.*, vol. 25, pp. 113-115, 1902), who showed that calcite actually has three cleavages:  $p\{100\}\{10\bar{1}1\}$ ,  $d^1\{10\bar{1}\}\{11\bar{2}0\}$ , and  $b^1\{110\}\{0112\}$ , the latter often wrongly considered as parting. According to the facility with which these cleavages can be produced, they can be listed as follows:  $p$ ,  $d^1$ ,  $b^1$ . The high density of the form  $d^1$  is thus accounted for.

considered equivalent, the structural lattice becomes simple cubic (with the parameters halved).

For chemical elements (in which all atoms are alike) one may expect the morphological and the structural lattices to coincide. From preliminary results obtained by one of us in an investigation now in progress, it appears that this is actually the case in most instances. Examples: Cu, Ag, Au, Al, Ge, Th, C (diamond), Si, Pb, Rh, Pd, Ir, Pt, all have the octahedron as their dominant form, hence their Haüy-Bravais lattice is face-centered; so is also their structural lattice.

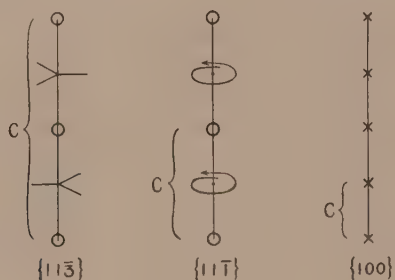


FIG. 1.

Schematic illustration of the relation between the three different lattices considered in the discussion of calcite.

The first figure represents the structure of calcite. Between the Ca-atoms (open circles) are indicated the positions of the  $\text{CO}_3$ -groups; they form equilateral triangles with the O-atoms in the corners: the two triangles are not structurally identical, but are turned  $60^\circ$  in relation to each other. The true identity period is therefore twice as great as the distance between two Ca-atoms. This corresponds to the lattice based on the form  $\{11\bar{3}\}$  of calcite.

The second figure shows that if the  $\text{CO}_3$ -groups were rotating (as for example the  $\text{NO}_3$ -groups do rotate in the high temperature modification of  $\text{NaNO}_3$ ) the period of identity would be only half as great as in the first case, corresponding to a lattice based on the form  $\{11\bar{1}\}$  of calcite.

The third figure shows that if the Ca-atoms and the  $\text{CO}_3$ -groups be regarded as geometrical points the identity period would be only one-quarter as great as in the first case, corresponding to a lattice based on the form  $\{100\}$  of calcite.

Aside from such meagre information, little is known about this challenging question of the relation between the external morphology and the intimate structure of crystals, which remains one of the principal problems of crystallography at the present time.



## STANDARDIZATION OF INDEX LIQUIDS

JEWELL J. GLASS\*

The determination of the indices of refraction of materials in standardized immersion liquids under a petrographic microscope has become the accepted method of mineral identification; has been very generally adopted for work with ceramic materials; and is gradually coming into use by chemists in the study of crystallized chemical materials. The rapidity with which optical methods may be applied, the small amount of material required, and the ability even to differentiate two or more distinct crystalline materials of identical chemical composition gives them very wide application in scientific and commercial determinations. The two most fundamental pieces of equipment for the application of these methods are a petrographic microscope and a set of accurately calibrated immersion liquids. The importance of immersion liquids is indicated by widespread discussion of the best materials and methods suitable for the preparation of such a set of index liquids. The petrographic laboratory of the United States Geological Survey has occasion to prepare and standardize as many as 50 sets of such liquids a year, and so the experience thus gained may be of use to others who have occasion to prepare such liquids.

Immersion liquids should be as nearly colorless as possible, and chemically stable. They should have as low volatility as possible, and when two liquids are to be mixed, the components should in general have equal or nearly equal rates of volatilization. If the volatility of both components is negligibly low, equal volatilization is not so essential, but liquids of very low index are unfortunately liquids of high volatility and it is advisable that these should have nearly equal rates of volatility. Each liquid should be miscible with the liquid lying immediately above or below, and it is desirable that the entire series of liquids should be completely miscible. A moderate degree of viscosity is also highly desirable, because with a viscous liquid both the mounted grains and the coverglass are better held in place and grains may be manipulated to bring them into suitable orientation without the violent agitation that otherwise often takes place when the coverglass is slightly moved. The liquid should be inert and not dissolve or react with the substance to be immersed. It is also desirable to use as small a number of

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components as possible, since then the various properties—indices of refraction, dispersion, and change with temperature—can be graphically expressed as simple curves between a few end members. Many mineralogists may have been deterred from attempting to prepare their own set of index liquids by the impression which seems to have gained ground that an elaborate technique is involved in the preparation of materials that fulfill the foregoing requirements. The fact is that easily procurable and relatively inexpensive index media are available over a wide range of indices of refraction, and that distillation and similar elaborate processes are quite unnecessary. Elaborate lists of materials to be used as index media have been described, but in fact better and more stable sets of liquids may be prepared from a few media.

A very large proportion of all mineral determinations involves the use of index liquids lying between 1.470 and 1.740, and fortunately liquids within that range that fulfill nearly all the foregoing requirements may be prepared from three components. The liquids lying between 1.470 and 1.630 are prepared by mixing medium Government oil and monochlor-naphthalene, and are almost colorless, slightly viscous, and remarkably stable; and those between 1.630 and 1.740 by the addition of methylene iodide to monochlor-naphthalene, and are pale honey-yellow, and slightly less stable. Since liquids may be prepared within this range (1.470–1.740) from only three liquids, all of their properties may be expressed by two sets of curves.

Medium Government oil<sup>1</sup> is an acid-free, colorless, odorless, and tasteless oil commonly used for instrument baths, such as immer-

<sup>1</sup> The liquids suggested may be obtained from dealers whose names are listed below.  
Medium Government oil, 1 gal. \$3.50.

Standard Oil Company of Indiana, Chicago, Ill.

Leeds & Northrup Company, 4901 Stenton Avenue., Philadelphia, Pa.

Halowax Oil No. 1007 (monochlor-naphthalene), 1 gal. \$5.00.

Halowax Corporation, Division of Bakelite Corporation, 247 Park Avenue,  
New York City.

Methylene iodide (MP) (No. 167), 100 grams \$5.00.

Methylene iodide (Pract.) (No. P-167) 1 kg. \$45.00.

Research Laboratory, Eastman Kodak Company, Rochester, N. Y.

Methylene Iodide, 1 lb. \$20.00.

Eimer and Amend, New York, N. Y.

Methylene Iodide, 1 lb. \$22.00.

Merck and Company, New York City.

Other liquids may be purchased from local dealers.

sion of resistance coils where a high degree of purity and stability is required. This oil has a viscosity at 100° F. of 95 to 100 seconds. Tests were made in this laboratory on the volatility of this liquid. A sample of 200 cc. was heated in open air at 70° C., and samples for index reading were taken every 12 hours for 276 hours. No change could be detected in the index of refraction (1.4658 at 24° C.), after cooling. The temperature was raised to 150° C. and held for 21 hours. The liquid became pale yellow in color but there was still no change in index of refraction after cooling. The remarkable stability of this liquid, together with its other favorable qualities, renders it a highly desirable index liquid. "Light" Government oil is less suitable as an index medium because it has a lower viscosity.

Monochlor-naphthalene (Halowax oil No. 1007) has an index of 1.6335 at 25° C. It is almost colorless and is miscible with the liquids above and below it. A 50 cc. sample of halowax oil was exposed to open air at room temperature for 44 days and was found to have changed from 1.6335 to 1.6345 at 25° C. A change of 0.001 under conditions much more extreme than those met in actual use is almost negligible.

Liquids suitable for index media in the low ranges of indices may be prepared from the liquids suggested below:

*n*-Decane (1.410) is a very satisfactory low-index liquid of low volatility, which may be used in combination with kerosene to cover a range of indices from 1.410 to 1.446, or with Government oil to 1.466. It is expensive, but 10 to 25 grams are sufficient for the preparation of a set of liquids. Butyl alcohol (1.399) may be combined with either kerosene or Government oil in the same way. For the range from 1.362 to 1.404 ethyl and amyl alcohol may be combined satisfactorily. The alcohols, however, are rather volatile and amyl alcohol has a disagreeable odor. A simple mixture of water (1.333) and glycerin (1.462) may be used for the low range of indices if the minerals are sufficiently insoluble. The ethyl-amyl alcohol and water-glycerin liquids, although solvents for some minerals that have indices within that range, can be used satisfactorily if measurement with them is made rapidly. Fortunately, the minerals which have indices in the low range, are rare in occurrence and few in number—mirabilite (1.395), fluorite (1.434), and opal (1.440) being among the few common ones. Fluorite and opal are the most common, both of which are insoluble in any of the liquids suggested for use in this range.



Liquids which have indices above 1.740 are less stable. Information on the preparation of high-index media can be obtained from a paper by H. E. Merwin.<sup>2</sup> The United States Geological Survey Bulletin 848, Microscopic determination of non-opaque minerals, (second edition) by E. S. Larsen and Harry Berman, quotes this information.

REFRACTIVE INDICES OF IMMERSION LIQUIDS

NAME OF LIQUID	$n$ at 23°C.	$\frac{dn}{dt}$	DISPERSION	REMARKS
Medium Government Oil	1.466	0.00035	Slight	Very stable. Mixed with Halowax oil gives range from 1.470 to 1.630.
Halowax oil no. 1007 (Monochlor-naphthalene)	1.633	0.0004	Slight	Mixed with methylene iodide gives range from 1.630 to 1.740.
Methylene iodide	1.737-1.740	0.0007	Strong	Discolors on exposure to light. Metallic tin may be added to prevent this change.
Medicinal mineral oil	about 1.470		Slight	May be used instead of Government oil.

The values of indices of refraction ( $n$ ) are for sodium  $D$ -line. The column marked  $dn/dt$  gives the change in index of refraction for each degree centigrade change in temperature. Index of refraction decreases approximately 0.00035 for 1°C., or 0.001 for 13°C., as the temperature increases.

The liquids should be kept in dropping bottles that have the combined ground stopper and dropper with glass cap. A 15 cubic centimeter bottle is the smallest that is sold by dealers, and that is larger than is required for the ordinary amount of work. It is best to keep the bottle half full, but with methylene iodide, economy suggests a smaller amount. A few grains of metallic tin should be kept in the bottles which contain methylene iodide in order that the free iodine which would darken the liquids may be taken up.

<sup>2</sup> Merwin, H. E., Media of high refraction for index determination with the microscope: *Jour. Washington Acad. Sci.*, vol. 3, pp. 35-40, 1913.

The bottles should never be allowed to stand without the stopper and cap in place, and the nearly light-proof container should be kept closed as light affects methylene iodide.

#### METHODS OF STANDARDIZING INDEX LIQUIDS FOR MEASURING INDICES OF REFRACTION

Where a few miscible liquids are to be mixed in various proportions in preparing a convenient range of index media, some accurate and easy method of measurement is necessary. Two methods of standardization have been used in this laboratory—namely, the method of minimum deviation with a hollow glass prism mounted on a one-circle goniometer, and the Abbe refractometer. With either of these methods the error of determination need not exceed  $\pm .00015$ . The refractometer is designed for the measurement of the indices of refraction and because of its simplicity and ease of manipulation it is very useful in measuring the low range of indices. The range of indices measurable with the standard type of instrument is 1.3000 to 1.7000. The refractometer yields quicker results than does the prism but it cannot be used for media which have indices higher than 1.7000. Liquids with high dispersion (above about 1.67) do not give clear shadow boundaries in the refractometer.

The method of minimum deviation with a hollow prism is not so rapid as that with the refractometer, but it can be used for the whole range of index media with a uniform degree of accuracy. C. S. Ross has designed a very satisfactory prism which is constructed by first grinding a rough glass prism, the approximate angle being determined by a contact goniometer. The hollow prism is made by cementing two parallel sided glass slides (12 by 25 mm.) to this base with bakelite, so that they project about 10 mm. above the base. The edges of the glass prism are cemented together with bakelite. The top of the basal prism is sloped inward so there will be less tendency for the drop of index liquid to escape. A prism angle of about  $45^\circ$  is a convenient size. Knowing the angle of the prism, determined by accurate measurement, using the formula

$$\frac{\sin \frac{1}{2} (\text{Prism angle} + \text{angle of deviation})}{\sin \frac{1}{2} (\text{Prism angle})}$$

a table should be constructed to show the angle of minimum deviation required to give any desired index of refraction.

## MONOCHROMATIC LIGHT SOURCE

The most satisfactory and convenient source of monochromatic light for the determination of indices of refraction of index media is a small helium gas tube. The helium gas tube, unlike the sodium flame commonly employed, may be used in an open lighted room without interference of air currents or outside sources of light. There is no appreciable radiation of heat; therefore, the position of the tube may be adjusted at close range to the goniometer signal slit. The tube lights instantaneously and maintains uniform intensity. The light given off is soft yellow-white, but on passing through the prism containing the index medium is split into seven well separated spectral lines. The yellow line,  $D_3$ , 5876Å, corresponds closely in value to the sodium line,  $D_2$ , 5890Å. The prominent red helium line, 6678Å, is relatively near in value to the lithium line, 6708Å; and the blue-green, 5016Å, and the blue-violet, 4471Å, of the helium are not far from the thallium, 5351Å, and the hydrogen, 4340Å. Thus, the helium gas tube from a single light source furnishes a light that gives principal lines almost uniformly distributed through the spectrum and includes wave lengths that may take the place of the commonly used sodium, lithium, thallium, and hydrogen sources of monochromatic light.

SPECTRUM OF HELIUM  
Wave lengths in Ångstrom units

Color	Wave length
Blue violet.....	4471
Blue.....	4713
Pale blue-green.....	4922
Blue-green.....	5016
Yellow.....	5876
Red.....	6678
Red.....	7065

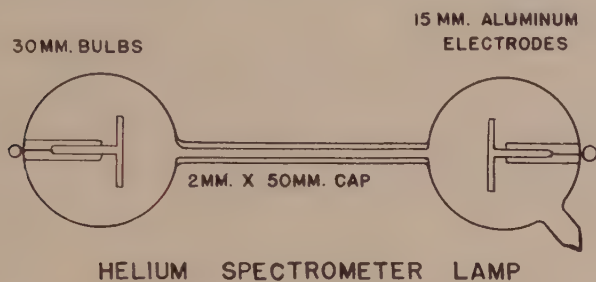
The helium lines may be used in the construction of a system of dispersion curves made by plotting the indices of refraction against the wave lengths of the conspicuous spectral lines in a similar way to that by R. D. Butler,<sup>3</sup> in which he used a hydrogen source and lithium, sodium, and thallium flames. A set of dispersion curves from which the index of refraction can be read to the fourth decimal place ( $\pm .0002$ ) has been constructed for the liquids described in

<sup>3</sup> Butler, R. D., Immersion liquids of intermediate refraction (1.450–1.630): *Am. Mineralogist*, vol. 18, pp. 386–401, 1933.



this paper and may be used to read the index of refraction of the liquids for any wave length.

The helium tube used by the Geological Survey was designed and made by P. G. Nutting.<sup>4</sup> As is illustrated in the accompanying sketch, the tube consists of two spherical bulbs 30 mm. in diameter connected by a straight piece of capillary tubing 50 mm. in length and 2 mm. bore. The electrodes are made of aluminum 1.5 mm.



thick and 15 mm. in diameter. These tubes are easily made by a skillful glass-blower and filled with helium gas at small cost. Helium gas has the advantage of withstanding a strong current for long periods of time.

The helium gas tube is best operated on a small potential transformer capable of delivering at least 20 milliamperes at 5,000 volts potential. The current is regulated by a lamp rheostat on the low voltage side of the transformer which is fed from ordinary A. C. mains. The current from a transformer connected in this way is not dangerous to handle, because the maximum current is limited by the resistance in the primary.

<sup>4</sup> Nutting, P. G., Luminous properties of electrically conducted helium gas: *Bureau of Standards Bull.*, vol. 4, 1907.

## SECONDARY SELENITE CRYSTALS IN TERTIARY STRATA IN TEXAS

M. N. BROUGHTON, A. & M. College of Texas.

### INTRODUCTION

Occurrences of selenite in the Tertiary formations of the Coastal Plain of Texas have been known for many years. Considerable discussion as to the origin and theoretical significance of these deposits has been advanced. As a result of early studies a number of hypotheses regarding the climates of the Tertiary epochs and geologic conditions under which the gypsum-bearing sediments may have been formed were advanced. Many early writers assumed that the selenite deposits were of primary origin. With this assumption the writer disagrees. Evidence derived from a study of one of these deposits which may be considered typical is presented in support of this contention. Interesting crystallographic features including numerous penetration twins and a rare crystal form, the positive hemiorthodome ( $\bar{1}03$ ), to which the letters *ee* are assigned are described and illustrated.

### DESCRIPTION OF OCCURRENCE

The selenite crystals here described are found on a branch of White Creek, three miles south of College Station, Texas. At this place erosion has produced a cliff about 30 feet high in which the crystals occur.

The section exposed is given below:

		Surface soil	3 ft.
		{ Cross bedded sandy clay	20 ft.
Pleistocene.	Terrace material	{ Basal conglomerate (pebbles 2 mm. to 1 cm. in diameter)	2 to 6 in.
Eocene.	Cockfield formation	{ Bedded, lignitic, clayey, porous sandstone	1 ft.

The detritus at the foot of the cliff is composed essentially of the same materials as the formations exposed higher on the cliff and has no doubt resulted from the slumping of these formations. The selenite crystals were first seen protruding from the dry surface of the detrital heap. The outer surface of the heap when dry forms a moderately hard surface composed of a matrix of sandy clay. On digging into this material one finds that the crystals decrease in

size and increase in numbers and in completeness of crystallization as depth increases. All gradations in size from minute specimens of microscopic size to the large skeletal crystals of about eight centimeters maximum dimension were found within a depth of approximately ten centimeters. The moisture content of the matrix also increases as depth increases. At the inner edge of the zone of crystallization the clayey sand was wet almost to the point of saturation. This condition indicates that calcium sulphate-bearing waters of the porous formations are slowly diffusing outward and subsequently evaporating, depositing near the surface crystals of selenite. The innermost margin of the zone of crystallization—a depth of approximately ten centimeters—is a plane determined by the loci of points at which the solution in its outward passage has lost a quantity of its solvent sufficient to reduce it to the point of saturation. Along this plane, which approximately parallels the outer surface of the matrix, precipitation is rapid, a large number of centers of crystallization are formed, and innumerable small crystals result. As the crystals are small and the supply of calcium sulphate is large, these crystals are completely developed. Moving progressively outward, diffusion and crystal growth become progressively slower and therefore larger crystals are produced. Development of the larger crystals has taken place first along certain crystallographic planes; while certain areas between these planes remain to be filled in. Development of crystals is then first as a skeleton which given sufficient time would no doubt result in a complete crystal.

The solvent bearing the calcium sulphate in solution is evidently vadose waters. Their abundance increases during rainy seasons and decreases during dry periods. The calcium sulphate in the waters is being dissolved from the underlying gypsiferous formations (Cockfield at this locality) through which it has been disseminated as the result of the chemical action of pyrite-derived sulphuric acid on the lime carbonate present in the form of fossil shells and lime nodules in some layers of this and similar formations. After every rainy period a thin, white powdery coating of gypsum may be observed on the face of cliffs of creeks of the vicinity. This coating is noticeable in a zone about four to eight inches wide about six inches to one foot above the level of the creek, and is presumably deposited from gypsiferous vadose waters percolating out of the porous formations along the water table in the valleys.

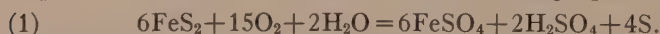


## CHEMISTRY

Numerous writers have discussed the origin of the gypsum in the Cockfield and similar lithologic units in the Coastal Plain. The best and most logical explanation of these deposits was given by Penrose in his discussion of the gypsum in the Fayette beds. His account of the formation of gypsum in these beds is quoted here.

... Sulphur and gypsum are of very frequent occurrence, the latter often being found as twin crystals in the shape of an arrowhead. The beds frequently contain carbonate of lime in the shape of nodules, or impregnating the strata. One of the most marked characteristics of the clays, and especially of the chocolate covered beds, is a white bleached appearance on the surface, while, a few inches in, they regain their dark color. This, and the presence of sulphur and gypsum, are intimately connected phenomena, and can be easily explained by the combined decomposition of the iron pyrites, carbonate of lime, and the vegetable coloring matter of the dark clays. The iron pyrites decompose with the formation of sulphate of iron and sulphuric acid; the sulphuric acid attacks the carbonate of lime, forming gypsum and carbonic acid; the former is deposited as crystals, and the latter goes in the air and surface waters. The sulphate of iron attacks the organic matter in the clays and is again reduced to iron pyrites with the evolution of sulphuretted hydrogen and oxygen. The oxygen forms carbonic acid with the vegetable matter, and rapidly goes off into the air. This reaction repeats itself until the clay finally becomes devoid of all vegetable material, and hence of coloring matter, and exposes a white surface. The sulphur, which originally formed a part of the sulphuretted hydrogen, but which has now lost its hydrogen, is deposited as a yellow or white crust on the surface and in the cracks of the strata.<sup>1</sup>

The oxidation of pyrite or marcasite, primary minerals of deposits rich in organic matter, to ferrous sulphate, sulphuric acid, and free sulphur is expressed chemically by the following equation:



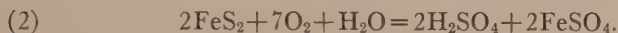
The formation of ferrous sulphate is confirmed by the presence of the mineral melanterite,  $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ , in the vicinity and at numerous other localities in these sediments. The production of sulphuric acid is proved by the presence of calcium sulphate in the form of gypsum. Sulphuric acid would be present as such only momentarily, as the lime carbonate in the sediments would immediately be attacked by any acid that might be introduced in the sediments from any source whatever. According to equation 1, it is theoretically possible for free sulphur also to be formed in the process of oxidation. When natural ferrous sulphides are powdered and

<sup>1</sup> Penrose, R. A. F., Jr., A preliminary report on the Geology of the Gulf Tertiary of Texas from the Red River to the Rio Grande: *Geological Survey of Texas*, E. T. Dumble, *First Annual Report*, Austin, 1899, p. 48.

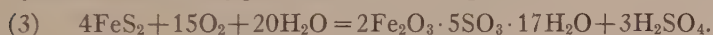
treated with nitric acid, a strong oxidizing agent, in a test tube, free sulphur is produced. *It has, however, been impossible to confirm the formation of free sulphur in the natural oxidation of these sulphides by its presence in enclosing sediments.*

No authentic report of free sulphur unquestionably identified as such occurring in these deposits has been found. It is reasonable to suppose that if sulphur had been present in the free state it would still be present as such at some localities. Tests on numerous sands and several brown shales which are impregnated with malantherite have failed to reveal the presence of native sulphur.

Due to the presence of malantherite and gypsum (derived from sulphuric acid) and the absence of sulphur, the following equation seems the more logical explanation of the decomposition of the iron sulphides:



A yellow coating occurring on rocks and in crevices in coastal plain sediments has been identified as the mineral copiapite,  $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$ . This mineral occurs in minute tetragonal crystals and ranges in color through several shades of yellow. It might have been easily confused with sulphur in the absence of confirmatory optical and chemical tests. Equation 3 indicates how the two compounds, copiapite and sulphuric acid, may be formed by the action of oxygen on the ferric sulphides.



Since the products called for in equations 2 and 3 have been confirmed by their presence or by the presence of their salts, it seems logical to accept these two equations as being the true expression of the processes in action in these sediments. *The formation of free sulphur is therefore open to question and cannot be definitely settled until observation confirms without doubt the actual presence of sulphur in the free state, or as a compound which is known to be derived in situ from free sulphur in these sediments.*

For the formation of gypsum from shell material or lime nodules the following equation may be written:



#### CRYSTALLOGRAPHY

All specimens show essentially the same forms although the degree of development varies in different individuals. The smaller

crystals exhibit more nearly complete development than do the large ones. The smaller crystals are elongated in the direction of the  $c$  axis while the large ones are elongated in the direction of the  $a$  or clino-axis. Figure 1 illustrates the forms recognized. In the illustration  $b$  is the clinopinacoid  $\{010\}$ ;  $m$  is the prism  $\{110\}$ ;  $l$  is the unit hemi-bipyramid  $\{111\}$ ;  $e$  is the positive hemiorthodome  $\{\bar{1}03\}$ ; (see also Pl. 2, Fig. 7, lower right); and  $ee$  is the positive hemiorthodome  $\{102\}$  (see also Pl. 2, Fig. 7, upper left).

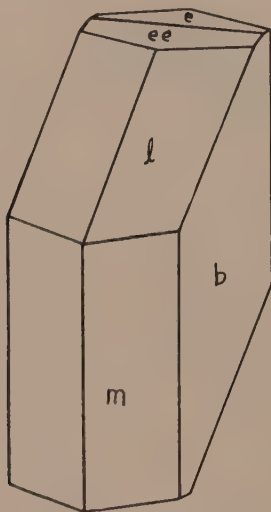


FIG. 1. Drawing illustrating crystallography of selenite.

Table I is a list of the forms present and crystallographic measurements made on them with a contact goniometer.

Cleavage is best developed parallel to  $b$  (010) and yields along this plane thin, polished folia with excellent glassy luster. Cleavage parallel to the direction of the plane (100) produces an irregular conchoidal surface. Many irregularities are present in these surfaces due to inclusions of foreign material. Cleavage fragments parallel to the plane  $(\bar{1}01)$  (form  $t$ , which is not present on these specimens) have a fibrous structure. The surfaces produced by this cleavage resemble the fibrous surfaces of satin spar.

Numerous inclusions of foreign particles are present in the crystals the most abundant of which are masses of clay and sand grains. One crystal was noted which had embedded within it a small



TABLE I. SUMMARY OF FORMS PRESENT AND CRYSTALLOGRAPHIC DATA

Form	Miller Symbols	Angular Relationships	Remarks
<i>l</i>	{111}	111/1 $\bar{1}$ 1 = 36°	Deeply concave in large skeletal crystals.
<i>m</i>	{110}	110/1 $\bar{1}$ 0 = 63° 30'	Moderately concave in large skeletal crystals.
<i>b</i>	{010}	110/010 = 56° 30'	Slightly concave in skeletal crystals.
<i>e</i>	{103}	edge 1 $\bar{1}$ 0—1 $\bar{1}$ 0/ $\bar{1}$ 03 = 87°	Rounded; convex. Very poorly developed. Not recognizable on large incomplete specimens.
<i>ee</i>	{102}	edge 1 $\bar{1}$ 0—1 $\bar{1}$ 0/ $\bar{1}$ 02 = 97°	Poorly developed on small specimens.

The form *e* (positive hemiorthodome 103), is barely recognizable on the forms on which it is best developed. This face is convex and rounded making the determination of its angular relationships with known crystallographic directions difficult and of doubtful accuracy. The angle which the form 103 makes with the interfacial edge 1 $\bar{1}$ 0—1 $\bar{1}$ 0—and hence with its parallel, the *c* axis—is 84°49'.<sup>2</sup>

Measurements made on a number of selenite crystals included in this study show a considerable range in value for this angle. These values are, however, well within the limits of error in measurements for an angle between such poorly developed forms. Determinations made on a selected few of the smaller specimens on which another face is fairly well developed yield a mean value for the angle made with the interfacial edge 1 $\bar{1}$ 0—1 $\bar{1}$ 0 of 97°. Calculations based on this value are suggestive of another positive hemiorthodome having the Miller symbols {102}. An examination of reference books on mineral crystallography shows the positive hemiorthodome {103} to be fairly common on crystals of selenite, while no case of the positive hemiorthodome {102} occurring on this mineral is recorded in these lists. According to Dr. Charles Palache,<sup>3</sup> this form has been reported by Cesaro on a crystal from Italy, but the form yielded only approximate measurements. In view of the fact that this form has not been designated by letters, the letters *ee* are now assigned to it.

The form *b* (010) is well developed on the small crystals and is moderately concave but well outlined by interfacial edges on the large skeletal forms. The forms *m* {110} and *l* {111} are also well developed on the smaller crystals and deeply concave, but well outlined by interfacial edges, on the larger skeletal specimens. Crystallization in the large skeletal forms has taken place along the symmetry plane (plane of the *a* and *c* axes) and from the center outward the following interfacial edges are developed:

*b*:*m*; *b*:*l*; *l*:*l*; *m*:*m*; and *m*:*l*, Plate 1. Figs. 1, 2, 3, 4, 5, and 6.

<sup>2</sup> Rogers, A. F., Introduction to the study of minerals, McGraw-Hill, New York, 1912, p. 36.

<sup>3</sup> Letter of Jan. 17, 1933 to J. T. Lonsdale.



PLATE 1.—Large skeletal, individual and twinned crystals of selenite.

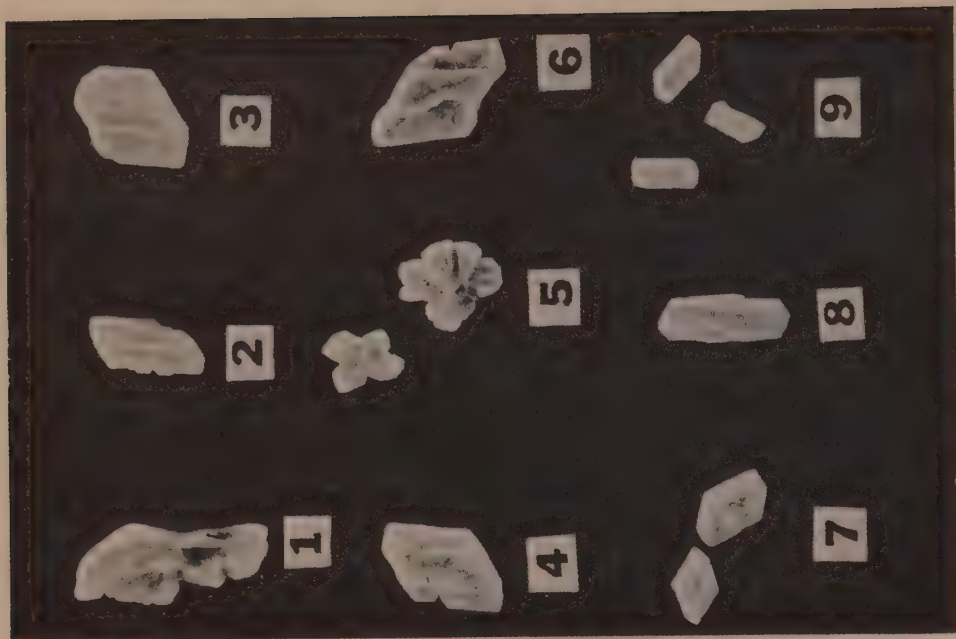


PLATE 2.—Selenite crystals: Figs. 1 and 6 skeletal crystals showing irregularities due to inclusions; Figs. 2, 3, 4, 7, 8, and 9 small completely developed crystals; Fig. 5 (upper left) complete.

well-rounded pebble of jasper, presumably derived from the conglomerate at the base of the terrace deposit. The clay and sand grains included in the crystals resemble the materials of the sediments in which the selenite crystals are found. The presence of these inclusions derived from enclosing deposits of Tertiary and Pleistocene ages is evidence favoring the contention that the selenite deposits are not primary in origin.

**TWINS.** Many of the selenite crystals are in the form of twins exhibiting essentially the same crystal forms as the single individuals described in the preceding section. Penetration twins forming crosses by the intergrowth of two individuals and rosettes by the intergrowth of more than two individuals are common. In some cases both individuals of the cross exhibit equal development, Pl. 2, Fig. 5., while in others one individual may be deficient in size in comparison to its twin, Pl. 2, Fig. 1. In a few specimens one end of an individual may be deficient in size in comparison to its counterpart on the opposite side of its twin, Pl. 1, Fig. 5. Rosettes formed by the development of from three to five individuals radiating from a common center are very conspicuous, Pl. 1, Fig. 5. All twins from this locality are considered to be paragenic in origin. It is clear that the different individuals of any group have developed from a common center of crystallization. The so-called "fish tail" twins (twinning plane 100) which are very common in Coastal Plain gypsum deposits and which are metagenic in origin were not found in the vicinity of this locality. The small crystal illustrated in Pl. 2, Fig. 5, upper left, is the nearest perfect twin found. It consists of two equally developed individuals one of which has been rotated through an angle of approximately  $45^{\circ}$ . The other crystal in the same figure is a deformed rosette of five skeletal crystals developed from a common center, four of which are in the same plane, while the fifth is perpendicular to that plane. Plate 1, Fig. 1, is a cross penetration twin (plane of 011) of two skeletal individuals with the end of one crystal broken off, while Plate 1, Fig. 4, illustrates a skeletonized cross twin with only one end of an inferior twin developed. Plate 1, Fig. 5, is a rosette of three approximately equally developed skeletal individuals, one of which is perpendicular to the plane of the other two.



# MONTICELLITE FROM CRESTMORE, CALIFORNIA

ROBERT S. MOEHLMAN AND F. A. GONYER, *Harvard University*.

## INTRODUCTION

The optical properties and chemical analysis of monticellite from Crestmore, California, are here given. This supplements the data given by Beliankin and Ivanov on "The System of Monticellite"(1).

Monticellite was suspected in rocks from Crestmore during the examination of specimens in which tilleyite was recently found and described by Larsen and Dunham (2). Concentration of the minute quantity of suspected monticellite from these specimens was undertaken by means of heavy liquids, but considerable difficulty was experienced in eliminating gehlenite, which corresponded very closely in density and index of refraction with the monticellite.

Finally, additional samples from Crestmore were obtained from the National Museum through the courtesy of Dr. W. F. Foshag, who had collected them. In these samples monticellite made up 75 per cent of the rock. Chemical analysis showed the mineral to be unquestionably monticellite with a composition close to the pure end member.

## OPTICAL PROPERTIES

The Crestmore monticellite differs from previously described specimens in having lower birefringence. The crystal form would also seem to be somewhat more distinct; there is a tendency for elongation parallel to the cleavage.

The optical properties of the Crestmore mineral are listed below, with those reported in Winchell's tables in the adjacent column for comparison. Sodium light was used in determining the indices. The optic angle was measured on the Fedorov stage.

	Crestmore	Winchell
Indices	$\alpha = 1.646$	1.651
	$\beta = 1.653$	1.662
	$\gamma = 1.659$	1.668
Birefringence	.013	.017
2V (—)	78°	75°
Dispersion	$r > v$	—
	distinct	
Orientation	$X = b$	$X = b$
Cleavage	{010} poor	{010} poor

## PHYSICAL PROPERTIES

The mineral is colorless, with greasy lustre. Specific gravity was determined as 3.083 by the quartz pycnometer; this was corroborated by measurement of specific gravities of the heavy liquids used in concentrating the mineral. Hardness of 5.5 and fusibility of 5.5 agree with data given by Dana. One direction of poor cleavage exists; this is not apparent in the hand specimen but in thin section is distinctly visible.

## CHEMICAL PROPERTIES

The mineral gelatinizes readily in hydrochloric acid. The analysis, by F. A. Gonyer, is given below, showing the mineral to be very close to the end member,  $\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ .

	Weight per cent	Mol ratios
$\text{SiO}_2$	37.46	624
$\text{FeO}$	3.98	55
$\text{MnO}$	0.52	7
$\text{MgO}$	22.78	569
$\text{CaO}$	35.20	628
$\text{H}_2\text{O}$	0.15	8
	<hr/> 100.09	

The properties of the Crestmore monticellite fit the graphs of Beliankin and Ivanov, filling a gap close to the pure, artificial mineral examined by Ferguson and Merwin (3).

## ASSOCIATION

In the specimens in which tilleyite was found, monticellite was present in minor amount, associated with spurrite, merwinite, wollastonite, gehlenite, tilleyite, garnet, and vesuvianite (4). In the specimens obtained from the National Museum, small garnet crystals are present in the monticellite and diopside is interstitial, moulding around the monticellite grains.

Eakle recorded monticellite in association with the brittle mica, waluwite, at Crestmore (5).

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## HEAVY MINERALS IN THE SYENITES OF PLEASANT MOUNTAIN, MAINE

WILLIAM F. JENKS, *Harvard University.*

In the course of petrographic work on material collected in 1931 on Pleasant Mountain, Maine, a qualitative study of the heavy minerals was made. The mountain, situated between Bridgeton and Fryeburg in the western part of the state, is held up by an oval-shaped stock of syenites, including nordmarkite, augite syenite, analcite syenite, and numerous porphyritic varieties of each of these.<sup>1</sup>

Observations were made with the following objectives in mind: (1) to determine what minerals are characteristic of each rock type, and hence get a broad idea of the variations within the stock as a whole; (2) to determine the degree of constancy of the heavy mineral suite within a given rock type; (3) to determine just how useful a qualitative mineralogical analysis of heavy minerals within a small stock such as that at Pleasant Mountain would be in correlation and identification of rocks whose relationship is in doubt.

*Method.* Of each sample selected for analysis a piece about a quarter the size of a hand specimen was ground to pass an eighty mesh screen. In addition two smaller meshes were used, the 160 and 250. Material which passed the 250 mesh screen was discarded, most of it consisting of feldspar particles. The two coarser grades were then passed separately through bromoform of a density approximating 2.9. After washing and drying the heavy residue a further separation was made with an electromagnet, the result being fairly clean concentrations of the various minerals. In general the magnetite was removed with a weak magnet, pyroxene, hornblende, biotite, and titanite with increasingly strong magnets. Apatite and zircon were non-magnetic.

<sup>1</sup> A paper by the writer on the petrography of the Pleasant Mountain intrusives will be published shortly in the *American Journal of Science*.



The greatest number of determinations was made on the nordmarkite, since it is the most extensive of the rocks. On most of the other types represented a single determination was deemed sufficient.

*Results.* The mafic minerals, biotite, augite, and hornblende, vary somewhat in relative and absolute proportion within a rock type, the nordmarkite being taken as an example. Between the different rock types there is a similar variation. Within the nordmarkite the amount of heavy concentrates varies from 3 to 11.7 per cent of the sample by weight. The most variable of the mafic minerals, augite, fluctuated from zero to about 17 per cent of the total heavies. Biotite and hornblende were more constant, maintaining together a proportion of 75 to 95 per cent of the heavy concentrates, the two minerals being present in about equal amounts.

TABLE I. TABLE SHOWING THE DISTRIBUTION OF THE HEAVY ACCESSORY MINERALS IN SOME OF THE ROCKS OF THE PLEASANT MOUNTAIN STOCK

	Titanite	Apatite	Magnetite	Zircon	Allanite
Augite syenites	a	a	a	vc	
Analcite syenite	a	c	vc	c	r
Monzonite and diorite	a	a	a	c	
Nordmarkite	a	a	a	vc	
Porphyritic hornblende					
syenite	a	a	a	vc	
Fine porphyritic syenite	a	a	a	s	
Coarse anorthoclase					
syenite porphyry	a	a	a	vc	

Explanation: a=abundant, vc=very common, c=common, s=scarce, r=rare.

Magnetite, apatite, titanite, and zircon were accessories in every sample examined. The only additional accessory is rare allanite, found only as nearly opaque and nearly isotropic dark red grains in the concentrate from the analcite syenite. In every rock but the analcite syenite the relative and absolute percentages of apatite, titanite and zircon remain fairly constant. For instance in the nordmarkite and anorthoclase syenite porphyry the non-magnetic concentrate was two to four per cent of the total heavy concentrate, and consisted of apatite and zircon in the ratio of about three to one. The samples from the analcite syenite, on the other hand, had a non-magnetic concentrate which was only 0.7 per cent of the total heavies, but the ratio of apatite to zircon was still ap-

proximately three to one. In the latter samples, however, the titanite was estimated to form six per cent of the total heavy minerals, whereas in the nordmarkite and other rocks examined titanite

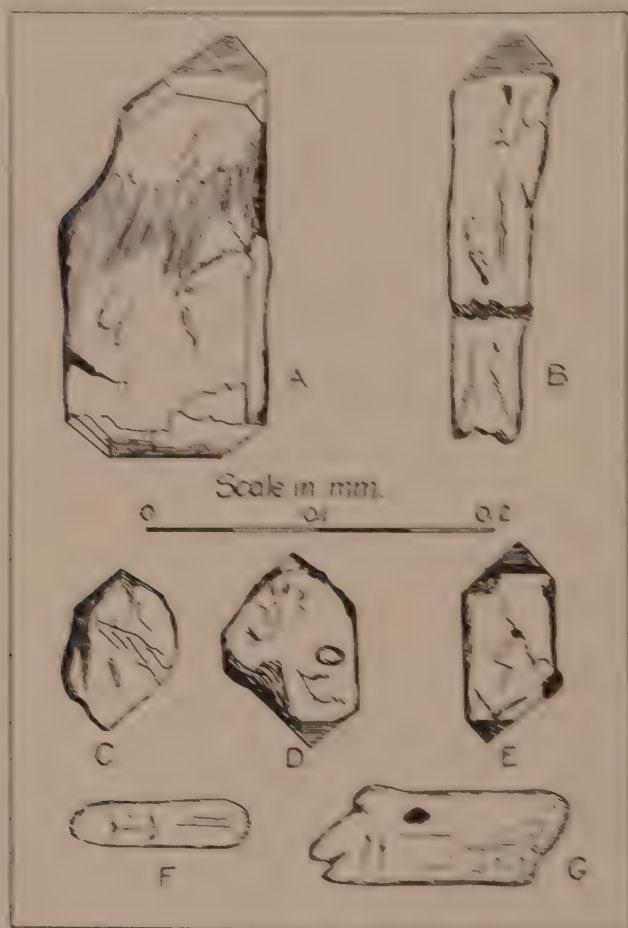


FIG. 1. Camera lucida drawings of zircon (A-F) and apatite (G and H) from heavy concentrates.

formed only about two per cent of the total heavies. Relative abundance of the various heavy accessory minerals in the several rocks of the stock are given in Table I.

The zircons, examples of which are shown in Figure 1, are color-

less or very light gray and commonly occur as euhedral, doubly terminated crystals. The usual forms are the first order prism and pyramid, with occasional development of the second order pyramid (see Fig. 1A). It was kindly determined by Professor A. C. Lane that the zircons in one sample are not radioactive. This fact is difficult of explanation, since the small zircons of igneous rocks are commonly more radioactive than the large ones. The titanite appears in the heavy concentrates as pale yellow-brown angular grains, while the apatites are long prismatic, in many cases with rounded or broken ends (see Fig. 1, F and G). Sometimes there is a trace of a basal termination.

*Conclusions.* As indexes of rock types the heavy accessories are practically useless. Not only do the relative and absolute proportions of the minerals vary almost as much within a rock type as within the stock as a whole, but the crystal habit and color are in addition practically invariant. This conclusion is only natural in a small stock where all the rocks are derived from a common magma within a relatively short interval of time. The interesting thing is that one rock of the series, the analcite syenite, should have a somewhat different combination of heavy minerals. Of little value to the petrographer, perhaps the mere listing of the accessory minerals will prove of use to students of sedimentation as a key to the provenance of any post-intrusive sediments that might be found in this part of New England.

NOTES AND NEWS  
CRYSTALLIZED NATIVE COPPER FROM  
FRANKLIN, NEW JERSEY

JOHN C. HAFF, *Columbia University.*

In the latter part of July, 1933, the writer found on the picking table at Franklin, New Jersey, an exceptionally large specimen of native copper. The ore from which the specimen came was being removed through the Palmer shaft. The actual level then being worked, or the mode of occurrence could not be ascertained. The mass is roughly rectangular in outline;  $10\frac{3}{4}$  inches (27 cm.) in length and  $5\frac{1}{4}$  inches (13 cm.) in width. Two octahedra of native copper are present at one end of the specimen, both being about 15 mm. in horizontal section. There are, moreover, several smaller octahedra of the same substance, possessing somewhat sharper terminations. Cleaned and trimmed, the nugget weighed 3056.5 grams, or, something over six and one-half pounds. Approximately one-quarter of the surface is encrusted with typical granular willemite-franklinite ore. Calcite, green copper carbonate, barite, and hodgkinsonite complete the mineral association. The latter mineral is relatively scarce at Franklin.

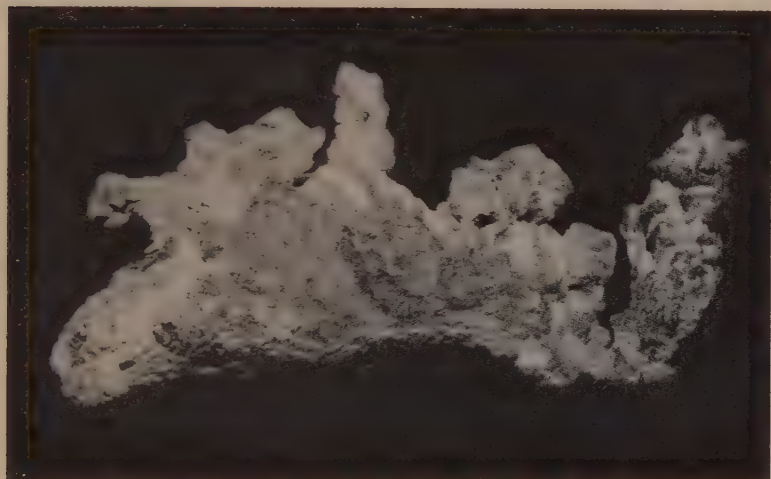
The willemite-franklinite mixture is in the form of a rather thin incrustation. It nevertheless possesses the definitely banded character so often seen in the massive granular ore. The willemite is of a very pale yellowish-green color and is strongly fluorescent. The white barite has crystallized in platy forms. The copper appears to be later than this mineral, and to bear a simple interstitial relationship to an intergrowth of barite crystals of prismatic habit. This can be demonstrated on only a portion of the specimen.

The hodgkinsonite has the characteristic rose-pink color, and exhibits a brilliant, clean cut cleavage parallel to (001) on the fresh surface. It generally occurs in massive form as an incrustation on the copper. However, one small crystal, about 6 mm. in thickness, is found in a recessed portion of the copper. The crystal faces are somewhat dull and etched, so that no reflections could be obtained. The optical properties of the hodgkinsonite are anomalous, and it was found convenient to identify it by comparison of x-ray diffraction patterns. The hodgkinsonite pattern was compared with a pattern of hodgkinsonite secured from one of the first specimens of



this mineral to be found at Franklin, now in the collection of the Department of Geology and Mineralogy, Columbia University.

Only one other known specimen of native copper comparable in size has hitherto been reported from Franklin. It is now in the U. S. National Museum. The specimen here described is not only unusual because of the size and crystalline character of the copper, it is of further interest to note the mineral association. In 1898 Wolff<sup>1</sup> described four occurrences of native copper from this locality. In each case the metallic copper was present in the form of



1 inch = appr. 3 inches

PHOTOGRAPH OF CRYSTALLIZED NATIVE COPPER FROM FRANKLIN

thin, fragile sheets and films. In two instances the copper occurred with the willemite-franklinite ore mixture, zincite, and calcite. Wolff noted that in these examples the copper films occupied seams bounded by slickensided surfaces, which was suggestive of dislocation and simple vein filling. In the remainder of his specimens the copper was associated with biotite, calcite, polyadelphite, and an "earthy light pink manganese mineral."<sup>2</sup> In 1913, Palache and Schaller,<sup>3</sup> in a paper describing the then new mineral hodgkin-

<sup>1</sup> Wolff, J. E., Occurrence of native copper at Franklin Furnace, New Jersey: *Am. Acad. Arts and Sci., Proc.*, vol. 33, pp. 430-431, 1898.

<sup>2</sup> Wolff, J. E., *Op. cit.*, p. 431.

<sup>3</sup> Palache, C., and Schaller, W. T., Hodgkinsonite, a new mineral from Franklin Furnace, N. J.: *Jour. Wash. Acad. Sci.*, vol. 3, p. 474, 1913.

sonite, remarked: "It occurs in seams in massive granular ore of the typical willemite-franklinite mixture; the seams are generally very thin with but a film of the mineral which is always associated with white barite and not uncommonly with plates of native copper." It will be noted that there is a very substantial similarity of association. It is not certain what mineral Wolff was referring to as "an earthy light pink manganese mineral," although this description is suggestive. On the whole, it appears that the association of barite, hodgekinsonite, and native copper at Franklin is normal. Other minerals, such as pyrochroite, axinite, and native lead, are also reported to occur with the three above.

Wolff<sup>4</sup> noticed the altered character of the garnet gangue on one of his specimens, and believed that the deposition of the copper might have been related to this change. He also pointed out that the copper was always later than the associated minerals, basing his conclusion on the fact that the seams are always bounded by fracture and gliding planes. Palache and Schaller<sup>5</sup> believed that the association and mode of occurrence of hodgekinsonite indicated a pneumatolytic origin for that mineral. This might also denote a pneumatolytic origin for the copper. In 1929, Palache<sup>6</sup> stated again that all three minerals, barite, hodgekinsonite, and native copper, are pneumatolytic in origin. Irrespective of classification, this new occurrence of native copper with its associated minerals, is additional evidence of their constant genetic relationship.<sup>7</sup>

<sup>4</sup> Wolff, J. E., *Op. cit.*, p. 431.

<sup>5</sup> Palache, C., and Schaller, W. T., *Op. cit.*, p. 475.

<sup>6</sup> Palache, C., Paragenetic classification of the minerals of Franklin, New Jersey: *Am. Min.*, vol. 14, no. 1, p. 11, 1929, and included table.

<sup>7</sup> I wish to acknowledge the interest manifested by Dr. Paul F. Kerr, Professor of Mineralogy, and the aid extended by him in the preparation of this paper.

METHODS OF HANDLING AND DETERMINATION  
OF DETRITAL GRAINS AND CRUSHED  
ROCK FRAGMENTS

FRANCIS C. PARTRIDGE, *Geological Survey, Union  
of South Africa, Pretoria.*

I read with interest in your April issue Mr. F. C. Calkins' contribution on the handling of grains under the microscope. Perhaps the methods used in South Africa might also interest your readers.

In the Mineralogical Laboratory of the Geological Survey of the

Union of South Africa, where identifications and estimations are made for the public, chemical quantitative methods have been found far too time-absorbing and expensive for this type of work. They have therefore been superseded by quantitative mineralogical methods combined with spectroscopic and micro-chemical tests on the individual grains. As most of these methods involve the separation and estimation of comminuted material, the handling and determination of small grains under the microscope form a large part of the work and have received much attention. The accuracy of some of the methods I am still busy investigating, and the results I hope to publish soon. The following method of handling and cleaning grains has been in constant use for over seven years and has been found the most convenient when much of this work has to be done. The methods of determination, however, have been constantly revised, and the method described for determining the indices more accurately has only recently come into use. It was originally a suggestion of Dr. S. van der Lingen, then at the University of Cape Town.

For picking out *dry minerals in air* a bristle from an ordinary pig-hair-hand-broom is used. A glass tube is drawn out until the bristle will only just fit in it, and the bristle is fixed with sealing wax. It is essential that the bristle should be firm and pliable but not springy. This also applies to the wire used for picking grains out of liquids. The grains are apt to spring away when accidentally pressed or moved, if hard and springy wires and bristles are used instead of pliable ones. The material of the bristle must also be slightly but not very absorbent to water, as experience has shown that this produces the necessary thin film on the bristle instead of a drop at the end of it. The tapering part of the tube to the end of the bristle is 5-6 cms., and the straight part of the tube at least 9 cms. in length. This enables it to be used like a pencil, the hand resting on the stage of the microscope. A bristle between  $\frac{1}{2}$  and  $\frac{1}{4}$  mm. is used. This is wetted with distilled water and brought into contact with the isolated mineral (a mere touch being all that is necessary). A steady hand, after practice, can lift grains without isolation; in fact grains are now seldom isolated for picking out when dry. The very small amount of water used soon dries and the mineral falls off. It is therefore necessary to place the mineral on a slide as soon as possible. If it does not fall off at once, it is easily removed by drawing the bristle gently over the slide. To ensure

complete dryness the slide is usually waved in the flame of a spirit lamp, but the micro-burner used by M. N. Short has now been found better. If preferred, a drop of water can be placed on the slide and the point of the bristle dipped into this, when surface tension removes the grain as the bristle is withdrawn from the drop. The grain must then be carefully dried. Care should be taken that the bristle is never used in oil or liquid other than water.

For *minerals in a liquid* a similar tube is used with a fine pliable wire instead of a bristle, e.g., copper wire from ordinary electric flex. When the grains are in water the wire is coated with vaseline; for their removal in other liquids a greasy or gummy substance insoluble in the liquid must be used. The wire is stuck about half an inch into a pot of vaseline and wiped by gently drawing over the inside of the pot until no vaseline is visible to the naked eye; the object being to get as thin a film of vaseline as possible on the wire. If a wire of about  $\frac{1}{4}$  mm. diameter is used the wiping is seldom necessary, but the top must be examined to see that a blob of vaseline is not sticking to it (as sometimes does occur). It is then very gently pressed on the grain. The wire with the adhering grain is dipped into a drop of benzol on a slide. Benzol is used rather than xylol because it is cheaper and evaporates quicker. The only difference is that xylol dissolves the vaseline rather more rapidly. For other greasy substances suitable solvents must be used. When the grain has fallen from the end of the wire it is rolled over a few times and pushed forwards or dragged to another part of the slide, before the benzol has evaporated, far enough away that the new drop of benzol, with which it is washed, cannot run into the old position. This procedure is repeated and the mineral then removed to a clean slide by the dry method. Two washings have been found to be quite sufficient to clean most grains. If one has not a steady hand, it is advisable to use the method of cleaning described for immersion liquids. A small cover is then placed on the drop of benzol after the grain has fallen from the wire and the procedure described in the next paragraph carried out. Grains of .05 to .5 mm. have been successfully handled in this way. This work is usually done on a dissecting stage under a binocular, but is also used with little loss of rapidity under a microscope.

For testing indices by immersion methods small glasses are cut with a sharp diamond from ordinary square cover-glasses. These are about 3 mm. square. They are rather troublesome to cut, but



it is well worth the trouble as they make the manipulation of individual grains much easier than large glasses. They can be made to serve almost indefinitely if they are scratched into spirits in a wide-necked bottle, after use. They can then be cleaned with  $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$  mixture, after pouring off the spirits, washed without handling in an evaporating dish, and dried by spreading on blotting paper. When these covers are used the area to be searched is small and the mineral is easily found. Less immersion liquid is used and cleansing of the grain is facilitated. The cover glass is touched with the immersion liquid and then placed on top of the mineral with a pair of forceps. To remove the liquid the cover-glass is tilted (i.e., merely pressed down on one side) and a clean piece of thin blotting or other absorbent paper placed in contact with the lower edge. The paper must have sharply cut edges and must not be torn. All but a minute fraction of the immersion liquid is rapidly absorbed when these small glasses are used. Benzol or some other quickly-evaporating solvent for the immersion liquid is then run under the cover-glass by means of a capillary tube. This is repeated three times, each drop of benzol being completely absorbed by blotting paper. Two washings usually suffice, but three will be better. This operation must be carried out on a flat surface and not in the hand as the cover-glass and mineral are liable to slip off the slide. The slide is then carefully held above the flame of a burner (Short's micro-burner has proved very much better) for a second, and any trace of liquid driven off. The slide cools in a few seconds and is ready for the next immersion liquid to be used.

When accurate indices are required the following method is used with the ordinary set of index liquids, from which mixtures are gradually being eliminated. A suitable grain is selected, if a Universal Stage is not available. When the oriented grain is found in polarized light to have an index just higher or lower than the liquid, a monochromater is substituted for the white-light used and the wave length varied until no bright line is seen on altering the focus of the microscope. The grain is washed, the next liquid, either higher or lower, substituted and the determination repeated. Indices are thus obtained in red and green or blue light. These are plotted on a graph and the index of the mineral in sodium light obtained by assuming that the index of the mineral varies in a straight line. The indices of the liquids are obtained by reading them from a

graph giving the index-wave-length curves of all the liquids in the set (their variation with temperature also being known). Where great accuracy is necessary or where the data for the liquid used are not known, a drop is placed in a prism and the index determined with the same wave-length of light and at the same temperature by the method of minimum deviation. With mixtures of liquids, where differential evaporation may occur, this index determination should always be made. We have found, however, that when correct containers are used for the liquids, this determination is only necessary about once a year.

When the optical properties of the grain have been ascertained, it is usually cleaned and tested microchemically for the main constituents of the mineral as indicated by the optical properties, after opening the mineral, if necessary, by the method used by P. C. Putnam, E. J. Roberts and D. H. Selchow (Contributions to Determinative Mineralogy, Part I, *American Journal of Science*, February 1928); or if enough of the grains can be found and picked out of the mass with certainty, 20–50 grains are selected, taken up in chemically pure sulphur, and tested spectroscopically.

For the general inspection of a sample nitrobenzol in a small shallow watch-glass, or uncovered on a slide, is used to cover grains instead of water, as this causes quartz and the feldspars to be practically invisible, and easily identified. As balsam and vaseline are slowly soluble in this liquid, seccotine is used to pick the grains out. Seccotine is very useful for this purpose. It is readily but slowly soluble in distilled water, and the grains are easily cleaned. The grain is therefore washed in water twice and finally in alcohol to hasten the drying. Seccotine can also be used with bromnaphthalene and methylene iodide and their mixtures. The pin of the tube is just covered with seccotine and the wire drawn over it. Nitrobenzol is a liquid strongly to be recommended to those working with crushed-rock grains or residues. Its index is near the higher index of quartz and its dispersion gives most quartz-grains red and blue borders under the microscope. It is also very useful for plagioclase feldspars—separating those commonly found in syenitic and granitic rocks from those found in basic and dioritic rocks. The nitrobenzol used has an index of 1.552 at 20°C. in sodium light.

*Thus:* a grain of feldspar showing any index > the liquid no matter what its orientation cannot have  $An < \pm 30$ .

If the indices of all grains of the plagioclase are  $>$  the liquid it is hardly likely to be  $< \text{An} \pm 44$ .

If the indices of all grains of the plagioclase are  $<$  the liquid it is hardly likely to be  $> \text{An} \pm 30$ .

If one index is greater and one less than the liquid then it is between  $\text{An} \pm 30$  and  $\text{An} \pm 44$ .

Therefore mere inspection of a crushed sample, in this medium, generally serves to identify an igneous rock or at least place it in its correct group. When more careful work is necessary the relative proportions of the constituent minerals are roughly estimated by areal or linear measurements. Grains of minerals other than quartz and feldspars are then selected from the sample and identified. From the properties and proportions of the minerals the rough composition of the rock is readily obtained. So far those results that have been checked against actual chemical analyses of the rock have shown good agreement. The crushed fragments are obtained by breaking pieces from different parts of the handspecimen, and crushed by sharp blows of a pair of two-inch-square hardened-steel plates.

An ordinary student's zoological set is very useful for accessory apparatus in this work. The scalpel is used for picking up samples of the crushed grains. The seeker is used for isolating grains by pushing them apart, and is also magnetized; the lancet is used for breaking off pieces of a mineral on the handspecimen; the forceps for handling cover-glasses, and the scissors for cutting the absorbent paper.

## NEW PUBLICATIONS

KURSUS DER KRISTALLOMETRIE, VICTOR GOLDSCHMIDT; HANS HIMMEL AND KARL MÜLLER. Gebrüder Borntraeger, Berlin, 1934, viii+167 pages, 183 text figures. 11.50 RM. bound.

Victor Goldschmidt, in his last years, gave considerable thought to the publication of a textbook describing the principles and methods of crystal measurement, projection, drawing, and calculation which he had developed.<sup>1</sup> The present volume is a laboratory manual, and follows closely the course<sup>2</sup> as given at Hauptstrasse Nr. 48.

Prefaced by 14 precepts (Arbeitsregeln), the introduction discusses the gnomonic, stereographic, and orthographic projections of crystals, and crystal measurement by means of the "Penfield" contact goniometer, and the Goldschmidt two-circle

<sup>1</sup> *Am. Mineral.* vol. 19, pp. 106-111, 1934. The Goldschmidt Two-circle Method; *Am. Mineral.*, 1921.

<sup>2</sup> Victor Goldschmidt Institut für Kristallforschung, Heidelberg.

instrument. A study of the crystals of quartz (Sutrop), garnet (Fort Wrangel), idocrase (Wilui), topaz (Brazil), feldspar (Pikes Peak), and copper sulfate, serves to ground the student in the general methods of sketching a crystal, projecting and drawing it; also the graphic determination of the face symbols, the polar elements, and crystal system. Likewise the cutting of plaster of Paris models is introduced here.

With this preparation, the intricacies of Goldschmidt's two-circle reflecting goniometer are described. By examples of typical crystals measured on this instrument: topaz (Thomas Mountain), realgar (Felsöbanya), calcite, (Egremont), phenacite (Brazil), anorthite (Vesuvius), idocrase (Vesuvius and Ala), and pyrite (Binnenthal), the methods of calculation of the polar and linear elements, and of an angle table are detailed. The treatment of twin-crystals is illustrated by examples of spinel (Ceylon) and epidote (Ober-Sulzbach).

The text is concise, but clearly written, and abundantly illustrated with good figures. Tables useful in making gnomonic projections (when charts are not available) are appended, and there is a brief index to the volume.

SAMUEL G. GORDON

COMPOSITION-TEMPERATURE PHASE EQUILIBRIUM DIAGRAMS OF THE REFRACTORY OXIDES. ROBERT B. SOSMAN AND OLAF ANDERSEN, Research Laboratory, United States Steel Corporation, Kearny, New Jersey. \$2.00 per set of four sheets.

The publication consists of four sheets, 24" by 19", reproducing in colors the four ternary composition-temperature diagrams of the four refractory oxides: silica, alumina, lime and magnesia. The scale is large enough to permit of interpolation to 0.1%. The base is a 500-millimeter equilateral triangle. The authors have recalculated the compositions and have replotted many of the original data of the Geophysical Laboratory, making minor revisions in the original diagrams to take account of later work, and have prepared the drawings by the same methods as are used for colored topographic maps. The base is in blue, temperature contours in green, compositions (including solid solutions) in red, and boundary curves and primary phases in black.

The sheets are now available at \$2.00 per set of four. Orders should be placed with the Research Laboratory, United States Steel Corporation, Kearny, New Jersey.

## PROCEEDINGS OF SOCIETIES

### NEW YORK MINERALOGICAL CLUB

#### *Minutes of the April Meeting, 1934*

A regular meeting of the New York Mineralogical Club was held on the evening of April 18th, 1934, at the American Museum of Natural History. The meeting was called to order at 8:15 p.m. by President Hawkins. The attendance was 75.

The speaker of the evening was the retiring President, Dr. Alfred C. Hawkins, who gave a paper illustrated with charts and lantern slides on the subject of "The Distribution of the Heavy Minerals in the Coastal Plain Sediments of New Jersey." Dr. Hawkins described the methods of elutriation, that is, the washing of the clay



through tanks with a controlled water flow. The heavy minerals remaining in each tank would then be examined. The percentages of the three minerals most constantly present (tourmaline, ilmenite, and zircon) were quantitatively determined by counts of grains under the microscope. The plotting of the resulting figures areally on the map according to the localities from which the original clay samples were obtained, shows that there is a systematic areal increase or decrease of the various proportions of these minerals; that their distribution indicates that the clays were deposited by some stream or other water flow coming in at the north-west corner of the present clay area, in the general drainage of the lower Raritan and Hudson rivers. A similar plotting of the total carbon contained in the various clay horizons gave similar results.

Then followed a period of questioning and discussions concerning the characteristics of clays.

DANIEL T. O'CONNELL, *Secretary*

*Minutes of Testimonial Meeting to Professor Edward  
Salisbury Dana on April 28, 1934*

A testimonial meeting of the New York Mineralogical Club in honor of Professor Edward Salisbury Dana, was held in the Maxwell Hall of the American Museum of Natural History on the afternoon of Saturday, April 28th, 1934. The meeting was called to order at 2:15 p.m. by President Gilman S. Stanton. The attendance was 90.

President Stanton introduced Dr. Alfred C. Hawkins, past President of the Club, who presented the engrossed certificate of honorary membership to Professor Edward Salisbury Dana, A.B., A.M., Ph.D., of Yale University. In the course of his remarks, Dr. Hawkins stated that the greatest monument which we might raise in memory of Professor Dana would be of slight consequence in comparison with the Sixth Edition of Dana's "System of Mineralogy," which came from the hand of Professor Edward Salisbury Dana.

Professor Dana modestly replied to the splendid tribute which Dr. Hawkins paid him, and proceeded to give all credit for his present reputation as a scientist to his father, James Dwight Dana, and his maternal grandfather, Benjamin Silliman. He traced the course of their lives and told how they had affected his own.

President Stanton then introduced Mr. Frederick I. Allen, past President of the Club, who spoke in praise of Professor Dana and his works, saying that "one of the happiest days of my life was the one on which I opened Dana's Textbook and Dana's 'System of Mineralogy' and that we see your face whenever we open a book with 'Dana' on the back."

The next speaker was Professor Alexander H. Phillips, Professor of Geology and Mineralogy at Princeton University. He also extolled the virtues of the 6th Edition of Dana's "System of Mineralogy," which he called the reference book of the world in mineralogy, in spite of the recently completed Hintze's extensive work in the German language.

The next speaker was Dr. Paul F. Kerr, who was also introduced by President Stanton. Professor Kerr told how, as he progressed in the field of mineralogy, he always found Professor Dana's books ahead of him. For the elementary student, Dana had written "Minerals and How to Study Them." One stage higher, he

found Dana's "Manual of Mineralogy." Still more advanced, he found Dana's "Textbook of Mineralogy," and finally, for the most advanced, Dana's "System of Mineralogy."

Dr. George I. Finlay, Professor of Geology at New York University, and author of a text on petrology and the study of rocks in thin sections, was next introduced by President Stanton. Dr. Finlay commented that Dana's "System of Mineralogy" was the Bible of the mineralogical field.

The last speaker was Dr. Bertram T. Butler, Professor of Geology of the College of the City of New York, who pointed out the great influence which Professor Dana has wielded over the youth of the country who have an interest in minerals.

The meeting adjourned, and the assembled members, accompanied by Curator Herbert P. Whitlock, retired to the Morgan Mineral Hall to view the collections there.

DANIEL T. O'CONNELL, *Secretary*

*Minutes of the Meeting of May 16, 1934.*

A regular meeting of the New York Mineralogical Club was held on the evening of May 16th, 1934, at the The American Museum of Natural History. The meeting was called to order by President Gilman S. Stanton. The attendance was 76.

Miss Catherine Schroder reported for the Membership Committee that their decision was favorable on the application of Mr. Charles H. Hale, Jr., of Kearny, N. J., and Dr. Frederic David Zeman, of New York, N. Y., and they were regularly elected to membership.

The speaker of the evening was Dr. Frank L. Hess, of the United States Bureau of Mines, Washington, D. C., who spoke on the subject "The Uranium and Vanadium Deposits of the Colorado Plateau." Dr. Hess pointed out that the important uranium and vanadium deposits of the United States are found in a great area of soft unaltered sandstones located in the Colorado Plateau, which lies between the Rocky Mountains on the east and the Wasatch Mountains on the west. The deposits are found scattered through an area stretching from Coal Creek and Blue Mountain in northwest Colorado southward and westward to Carrizo Mountain just south of the "Four Corners" where Colorado, Utah, Arizona, and New Mexico meet. In Utah, they are found along the east side of the San Rafael Swell, in the Henry, Blue, and LaSal Mountains. Within this area, there are long distances through which no deposits are found, however.

The principal uranium mineral is carnotite, usually found as a bright yellow powdery mineral disseminated through the sandstones. The Navajo Indians who lived in the vicinity are believed to have been the first to use this mineral, which they used to make a black dye. Although carnotite was probably recognized by the early prospectors, it had no value until 1898, when Gordon Kimball, a mining man of Telluride, Colorado, gave some of the yellow mineral to a French chemist named Poulot, who determined that it contained uranium. It was not yet known that the mineral also contained radium, which was discovered in the same year. Poulot passed specimens on to Friedel and Cummengé in Paris, who found the substance to be a new hydrous potassium uranium vanadate, and they named it carnotite for the French chemist, Adolphe Carnot. Later, the green color of the LaPlata sandstones near Placerville, Colorado, was found to be due to the presence of vanadium.



Dr. Hess then discussed in detail the uranium and vanadium deposits in the several formations found in the vicinity, beginning with the Shinarump conglomerate, which contains quantities of fragmental tree trunks and boulders in cross-bedded sand. Part of the sand is made up of asphaltite grains. This asphaltite carries both uranium and vanadium.

Dr. Hess also described the so-called "butter balls," which are small masses of very pure carnotite.

Dr. Hess described his discovery of several minerals, including rauvite, a purplish massive uranium and vanadium mineral, uvanite, a mineral which corresponds closely to carnotite without potassium. He also found torbernite (copper uranium vanadate), halotrichite (iron aluminum sulphate) and a little erythrite the cobalt bloom.

Dr. Hess then continued with a description of deposits found in the LaPlata sandstones, which lie above the Shinarump conglomerate stratigraphically. A thin, unevenly bedded limestone divides the formation into two parts and immediately below the limestone large flat lenses of the sandstone are cemented by the vanadium mica roscoelite, which gives them a dark green color. The lenses are enclosed within sandstone of a light green color, due to mariposite, the chromium-bearing muscovite. Directly above the LaPlata formation is the Morrison formation, containing most of the carnotite deposits, which, from 1907 to 1920, furnished most of the world's radium. The deposits in all cases are found in the vicinity of plant remains in this formation. The commonest mineral in all the deposits is roscoelite, but instead of being greenish as in the rocks below, it is gray or black.

On the south side of Paradox Valley, near its head, masses of sandstone are colored black by the mineral vanoxite, which forms tiny prisms between the sand grains. At other places, the sandstone is impregnated with spots of carnotite and others of vanoxite, and such ore is known to the miners as "rattlesnake ore." No carnotite deposits are found in the Morrison formation without vegetal matter, except where they can be shown to have been moved by percolating waters. Dr. Hess called it a shallow inland sea, with organic matter which trapped the metals as they weathered from the old veins, of which even the roots have disappeared. The waters draining the slopes leading to the lake or sea reached the veins found in the rocks and carried small amounts of uranium, vanadium, pyrite, chalcopyrite, and other minerals down. The oxidation of sulphides would form sulphuric acid, which would dissolve the uranium and vanadium and carry them into the lake, probably accompanied by some selenides.

After Dr. Hess concluded his talk, a period of question and discussion followed, participated in by Mr. I. O. Lee, Dr. Blank, Mr. Allen, and Mr. Radu.

DANIEL T. O'CONNELL, *Secretary*

## NEW MINERAL NAMES

### Graebite

ALFRED TREIBS AND HERMANN STEINMETZ: Über das Vorkommen von Anthrachinon-Farbstoffen im Mineralreich (Graebeit), *Justus Liebigs Annal. Chem.*, vol. 506, 171-195, 1933.

CHEMICAL COMPOSITION: A polyhydroxyanthraquinone, about  $C_{18}H_{14}O_8$  or  $C_{17}H_{14}O_8$ . Analysis on pure orange red crystals (1.285 mgs.) C 55.71, H. 3.18. Soluble in chloroform and benzol-ligroin. M. P. 245°.

CRYSTALLOGRAPHICAL PROPERTIES: Small prisms with parallel extinction and pleochroic—parallel to the prism, weak, across the prism distinct red. After recrystallization from acetone prisms with inclined extinction result.

OPTICAL PROPERTIES: Color red, orange red after sublimation. Absorption spectra and fluorescence spectra given. Dyes wool.

OCCURRENCE: Found as red stains in blocks of shale bearing plant remains in a fault zone at Olsnitz, Saxony, at a depth of 291 meters. Believed to be a natural compound and not the remains of explosives or the effect of microorganisms on decaying mine timbers.

W.F.F.

#### NOMINATIONS FOR OFFICERS OF THE MINERALOGICAL SOCIETY OF AMERICA FOR 1935

The Council has nominated the following for officers of *The Mineralogical Society of America* for the year 1935:

PRESIDENT: Clarence S. Ross, United States Geological Survey, Washington, D. C.

VICE-PRESIDENT: J. Ellis Thomson, University of Toronto, Toronto, Ontario.

SECRETARY: Paul F. Kerr, Columbia University, New York City.

TREASURER: Waldemar T. Schaller, United States Geological Survey, Washington, D. C.

EDITOR: Walter F. Hunt, University of Michigan, Ann Arbor, Michigan.

COUNCILOR (1935–1938): John F. Schairer, Carnegie Institution, Washington, D. C.

The fifteenth annual meeting of the Society will be held December 27–29, 1934, at the University of Rochester, Rochester, New York. It is planned to publish in the December issue of the *Journal* a *preliminary* list of titles of papers to be presented before the Society at its annual meeting. In order to appear on the advance program, titles of papers should be in the hands of the Secretary by *November 10*.

PAUL F. KERR, *Secretary*

#### Correction

In the Memorial of Georges Friedel, by J. D. H. Donnay (*Am. Mineral.*, vol. 19, pp. 329–335, 1934), page 331, lines 23 and 24, *instead of*: “on an allotropic transformation of diamond into graphite,” *read*: “on an allotropic transformation at high temperature distinct from the transformation of diamond into graphite.”